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The Measurement of the Conductivity of Electrolytes in Very Dilute Solutions

THE MEASUREMENT OF THE CONDUCTIVITY OF ELECTROLYTES IN VERY DILUTE SOLUTIONS

BY

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B. S. University of Rochester, 1913

M. S. University of Illinois, 1915

THESIS

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IN

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Henry J Weiland

ENTITLED The measurement of the conductivity of electrolytes in very dilute solutions

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

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I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

In the theoretical discussion of many chemical systems it is necessary to know the concentrations of both the ions and the non-ionized molecules. These concentrations are calculated from the degree of ionization α. For uni- univalent electrolytes α is best given by the equation $\alpha = \frac{\Lambda_c}{\Lambda_o} \cdot f\frac{\eta_c}{\eta_o}$ where Λ_c is the equivalent conductance at the desired concentration and Λ_o is the value of the equivalent conductance at infinite dilution. $f\frac{\eta_c}{\eta_o}$ is some function of the viscosity of the solution the value of which in sufficiently dilute solutions may be taken as unity.

An error of 0.1 % in the value of Λ_o will produce the following error in the calculated concentration of the undissociated molecules.

Table I

Concentration of salt Moles per Liter	% error in the calculated concentration undissociated molecules
0.01 N	1.7
0.001 N	5.8
0.0001 N	25.

Since a small error in the Λ_o value produces such a large error in the calculated value of the concentration of the unionized molecules in the solution, it is quite necessary to determine the value as accurately as possible. This value is usually determined by some method of extrapolation from the Λ_c values in dilute solution, for the Λ_o value itself being a limiting one cannot be measured experimentally. The best that can be done is to base this extrapolation on the assumption that the functional relation between equivalent conductance and concentration which is found to hold at the lowest measured concentrations continues to hold down to zero concentration.

There are many empirical formulas recorded in the literature for expressing the relation of the equivalent conductance to the concentration over that concentration range within which reliable measurements can be obtained. In the case of weak electrolytes the Ostwald Dilution Law (1),

$$\frac{\left(\frac{\Lambda_c n_c}{\Lambda_o n_o}\right)^2 C}{1 - \frac{\Lambda_c n_c}{\Lambda_o n_o}} = K_E$$

holds true in a large number of cases (2). In the case of strong electrolytes, however, the Ostwald Dilution Law does not hold. Such substances as the strong mineral acids, strong bases, and uni-univalent salts do not obey the same laws as do the weak electrolytes.

Among the many empirical formulas which have been put forward in an attempt to obtain a serviceable relation between the equivalent conductance and the concentration of the strong electrolyte in solution, the most important are those of ; Kohlrausch (3), Rudolphi (4), Van't Hoff (5), Storch (6), Arrhenius (7), Kraus and Bray (8), and Bates (9). Much discussion of these various equations can be found in the literature so that it is hardly necessary to enter further into it here. It seems advisable, however, to bring into a systematic form (Table II) a comparison of the results of these equations with the data for a single salt, potassium chloride at 18°C, so as to indicate the degree of concordance between the various equations and the experimental data in the dilute solutions. The equations of Rudolphi, Van't Hoff, and Storch can be shown to be practically mathematically identical with that of Kohlrausch, so that the values for the latter equation only are tabulated in this group.

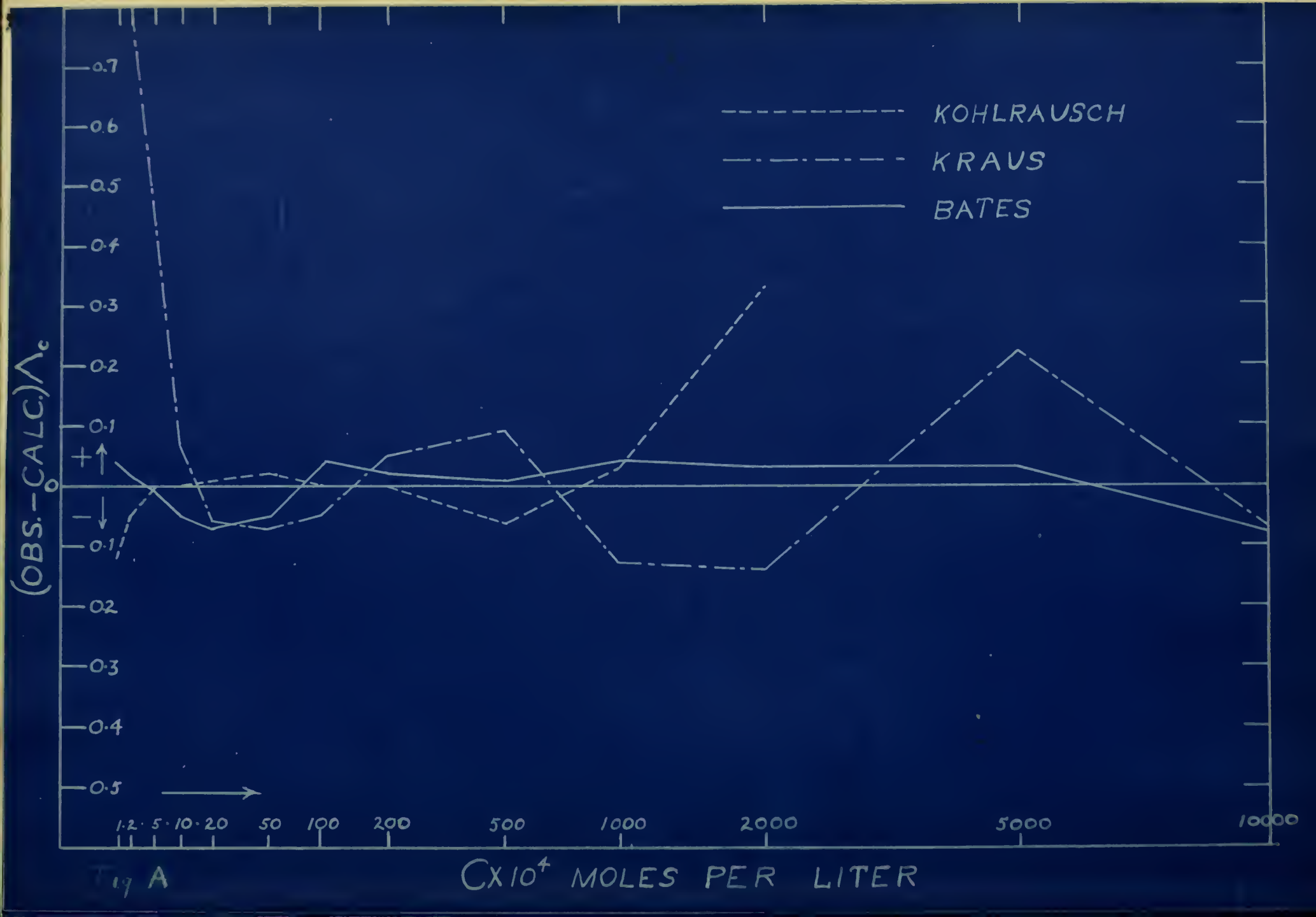

KOHLRAUSCH
KRAUS
BATES
(OBS.-CALC.)Λ_c
0.7
0.6
0.5
0.4
0.3
0.2
0.1
+
0
−
0.1
0.2
0.3
0.4
0.5
1·2·5·10·20
50
100
200
500
1000
2000
5000
10000
C X 10^4 MOLES PER LITER

Fig A

TABLE II

Concentration Moles per Lit.	Observed Kohlrausch Λ_c ****	---Calculated----- Kohl. Λ_c ***	Kraus. Λ_c **	Bates. Λ_c *	(Observed-Calculated) Kohl.	Kraus.	Bates.
0.0	.	130.03	128.5	129.50	.	.	.
.0001	129.00	129.12	128.1	128.96	.12	.9	.04
.0002	128.70	128.75	127.9	128.68	.05	.8	.02
.0005	128.04	128.04	127.6	128.05	.00	.44	.01
.001	127.27	127.27	127.2	127.32	.00	.07	.05
.002	126.24	126.23	126.3	126.31	.01	.06	.07
.005	124.34	124.32	124.41	124.39	.02	.07	.05
.01	122.37	122.37	122.42	122.34	.00	.05	.03
.02	119.90	119.90	119.85	119.88	.00	.05	.02
.05	115.69	115.75	115.60	115.68	.06	.09	.01
.1	111.97	111.94	112.10	111.93	.03	.13	.04
.2	107.90	107.87	108.04	107.87	.33	.14	.03
.5	102.36		102.14	102.33		.22	.03
1.	98.22		98.167	98.299			.08

**** Values obtained from data of Kohlrausch, corrected to Atomic Weights of 1911 by Noyes and Falk.
Journal of American Chemical Society Vol. 34. page 461.

*** Kohlrausch Equation for Calculations, values corrected to 1911 Atomic Weights.

$$\frac{\Lambda_o - \Lambda_c}{\Lambda^p} = K C^{1/2}.$$

$\Lambda_o = 130.10$, $p = 3.20$, $1000\ K = .010870$ } For old atomic weights.

Sitzungsberichte der Akademie der Wissenschaften zu Berlin 1900 Vol. II page 1002

** Kraus Equation

$$\frac{\left(\frac{\Lambda_c n_c}{\Lambda_o n_o}\right)^2 C}{1 - \frac{\Lambda_c n_c}{\Lambda_o n_o}} = K + K' \left(\frac{c\,\Lambda_c}{\Lambda_o}\right)^h$$

$\Lambda_o = 128.3$, $K = 0.080$, $K' = 2.707$, $h = 0.783$

Journal of American Chemical Society Vol. 35 page 1412.

* Bates Equation

$$\log_{10} \frac{\left(\frac{\Lambda_c n_c}{\Lambda_o n_o}\right)^2 C}{1 - \frac{\Lambda_c n_c}{\Lambda_o n_o}} = K + K' \left(\frac{c\,\Lambda}{\Lambda_o}\right)^h$$

$\Lambda_o = 129.50$, $K = -3.7905$, $K' = 4.020$, $h = .0775$

Principles of physical Chemistry, 1st, p. 216. Washburn.

As may be seen in Table II and the accompanying figure A, each of these equations expresses the experimental data more or less satisfactorily in certain parts of the curve. However in that part of the curve where reliable experimental data are not at hand each of the equations differs from the others. Owing to the fact that the determination of the Λ_o value is influenced largely by the experimental values of Λ_c in the most dilute solutions, it is necessary to know the Λ_c values very accurately over the concentration range 0.001 N to 0.00001 N. Values at a concentration 0.0001 N and below are unreliable, irregular and inconsistent. Even the values at 0.001 N for potassium chloride have been challenged by some, (10) due to the possible error in applying the "water correction".

It is the purpose of this investigation to obtain values of the equivalent conductance of potassium chloride at 18°C over the concentration range 0.001 N to 0.00001 N. The work naturally divides itself into the following problems:

1st. The preparation of a better conductivity water.

2nd. The arrangement of a cell suitable for the measurement of the dilute solutions out of contact with the atmosphere.

3rd. The application of a correction if necessary to the concentration of the solutions due to adsorption effects.

II

PREPARATION OF CONDUCTIVITY WATER

PREPARATION OF CONDUCTIVITY WATER

As just stated, one of the probable sources of error in the determination of the conductivity of the more dilute solutions is the correction which should be made for the conductance of the water. In the case of neutral salt solutions it is customary to merely subtract the specific conductance of the water from the total conductance in order to get the conductance of the salt. Thus Kendall (11) concludes that " Substantially accurate results are obtained by the method of Kohlrausch, direct subtraction of the water conductivity." In the case of acids, bases and basic salts however, the correction is a more complicated procedure. Thus according to Kohlrausch (12),"Säuren, Basen und alkalisch reagirende Salze (Karbonate) kann man überhaupt nicht mit Erfolg in äusserster Verdünnung untersuchen. Die allerersten kleinen Mengen, die man dem Wasser zufügt, geben beträchtlich kleinere Vermehrungen des Leitvermögens als die späteren Mengen, bei schlechtem Wasser sogar zuweilen Verkleinerungen; das Äquivalentleitvermögen wächst scheinbar im Anfange, während dasselbe bei allen neutralen Salzen immer abnimmt). Die Depression in grosser Verdünnung ist mindestens zum Teil sekundär, da sie im so kleiner ausfällt, je reiner das Wasser ist. Der Umstand, dass die Verunreinigungen aus der Atmosphäre (Ammoniak, Kohlensaure) selbst schwache Basen oder Säuren sind, scheint die Ursache zu bilden."

Assuming in the case of neutral salts that the conductivity of the water can be merely subtracted, then the smaller the correction which has to be made for the water the greater will be the probability of obtaining a true value for the specific conductivity of the salt. Below are tabulated the water corrections necessary with a neutral salt, potassium chloride at 18° C, at different concentrations using water of a specific conductivity, 1×10^{-6}, 0.06×10^{-6},

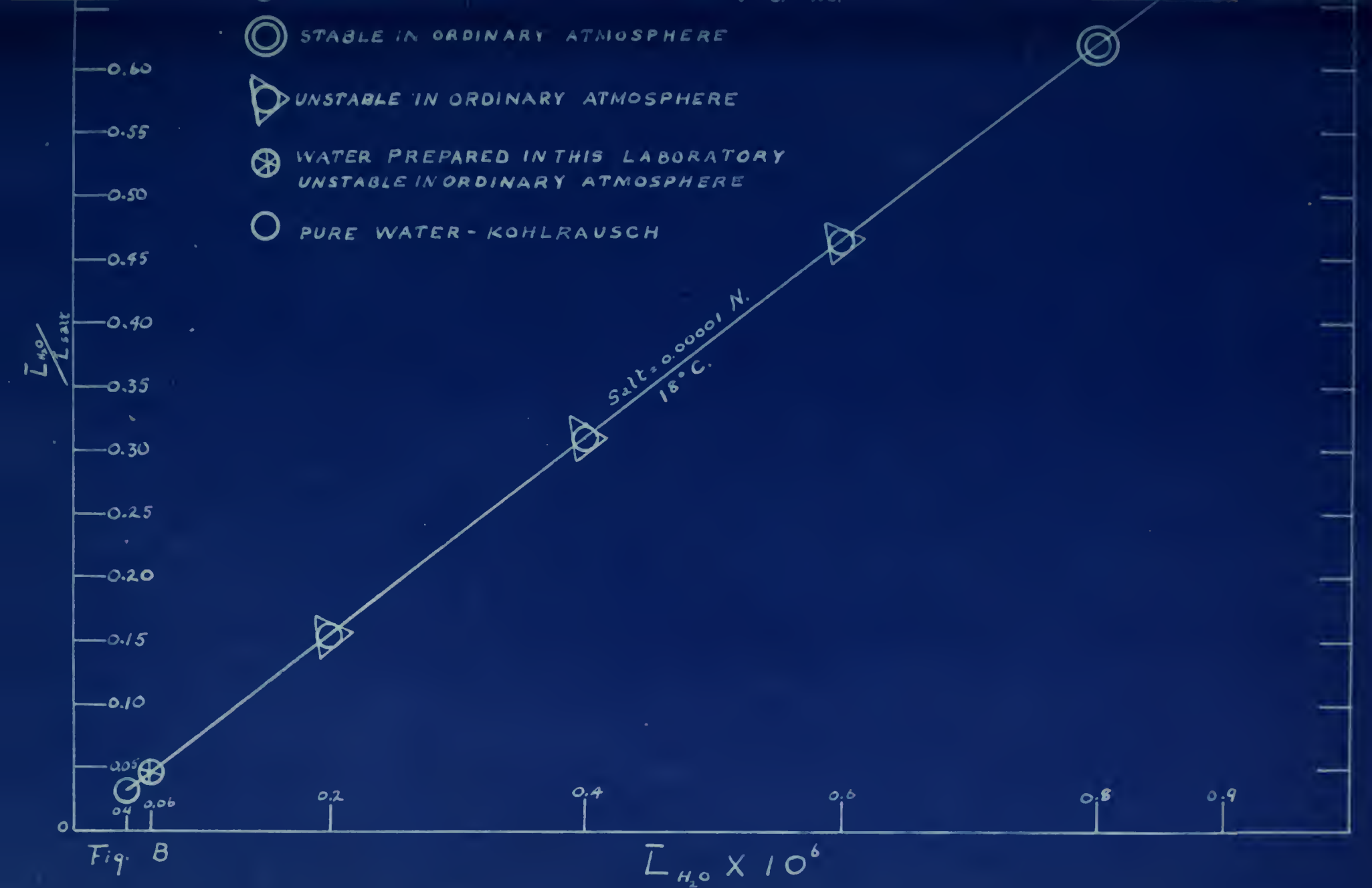

STABLE IN ORDINARY ATMOSPHERE
UNSTABLE IN ORDINARY ATMOSPHERE
WATER PREPARED IN THIS LABORATORY
UNSTABLE IN ORDINARY ATMOSPHERE
PURE WATER - KOHLRAUSCH
Salt = 0.00001 N.
18° C.
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0.04
0.06
0.2
0.4
0.6
0.8
0.9
$\frac{L_{H_2O}}{L_{salt}}$
$L_{H_2O} \times 10^6$

Fig. B

and 0.04 X 10^{-6} respectively.

Table III

Concentration of salt in Moles per Liter	Specific Conductivity X 10^{6}	Equivalent Conductance	% Correction for Conductivity of the Water		
			1 X 10^{-6}	.06x10^{-6}	.04x10^{-6}
1 X 10^{-6}	.129	129.5 *	886.	31.	24.
1 X 10^{-5}	1.294	129.45 *	44.	4.4	3.
1 X 10^{-4}	12.9	129.00	7.7	.46	.31
1 X 10^{-3}	127.3	127.3	.78	.047	.031
1 X 10^{-2}	1224.	122.4	.082	.0049	.003
1 X 10^{-1}	11200.	112.0	.009	.00054	.00036

* Values from Bates Equation.

It is to be noticed in Table III that the percentage correction for the conductivity of the water in dilute solutions is very large in the case of water having a specific conductivity of 1x10^{-6}. However a large amount of the best conductivity data recorded in the literature has been obtained from experiments in which the water used was of the above value. Attention is called to the fact that the difference between the percentage corrections in the case of water with a specific conductivity .06 X 10^{-6} and of water with a specific conductivity of .04 X 10^{-6}, practically pure water, is very small. There is therefore practically no advantage to be gained in attempting to prepare water having a specific conductivity less than .06x10^{-6}.

If water of a specific conductivity lower than 0.8 X 10^{-6} at 18°C is used, there is a large possibility of contamination during handling unless special precautions are taken. Contamination of the water may be due to three causes: first, the solubility of the vessels which are used; second, the contaminations due to the carbon

dioxide, ammonia etc. of the atmosphere (13) ; third, the adsorption of electrolyte from the electrode. Even in the transferring of water from one vessel to another except with the greatest care the specific conductivity of the water may rise from 0.35 or 0.3 X 10^{-6} to 0.6 X10^{-6}. Thus Kohlrausch and Maltby (14) state, " That even tho exact measurements of .00001 N solutions can be made, the change of specific conductivity due to the pollution of the water is relatively so high that one can no longer attach any significance to the results." According to Kendall (15) the observed conductance of good conductivity water (0.5- 0.8)X 10^{-6} at 18° C is entirely due to carbon dioxide from the air. He has considered the equilibrium of the system, carbon dioxide and water, and calculated that the solubility of carbon dioxide in water at the average partial pressure it has in the atmosphere is enough to give the water the above conductance. The proper correction for the conductance of water therefore becomes a vital question when dilute solutions are considered.

ATTEMPTS AT PREPARATION OF CONDUCTIVITY WATER

The classical case of the preparation of water of the highest degree of purity is that of Kohlrausch and Heydweiller (16). This research was not directed toward the obtaining of a quantity of water sufficient for carrying on conductivity measurements with salts but rather to obtain a value for the specific conductivity of pure water itself. Their process consisted of distillation in a closed evacuated system. The enclosed system consisted of two vessels, made of glass, one of which held the electrodes. The water was distilled back and forth from one chamber to the other by alternate heating and cooling of the two chambers. The initial filling of the apparatus was made with water having a specific conductivity of 0.7 X 10^{-6}. The specific

conductivity of the water upon evacuation of the apparatus fell to 0.25×10^{-6}. The repeated distillation of this water back and forth in the apparatus for a period of a month, a process consisting in all of 42 distillations gave water with a minimum conductance of 0.043×10^{-6} mhos. at 18° C. The quantity of water prepared in this way was but a few cubic centimeters, not a sufficient quantity to be used in the measurement of the conductivity of salt solutions.

In 1908 Hartley, Campbell and Poole (17) in their study of dilute solutions required a high grade of conductivity water. They designed a still which was the outcome of a number of suggestions gathered from other laboratories in England. By means of it they were able to obtain 2½ liters of water having a specific conductivity 0.75×10^{-6} and 3 liters 1.5×10^{-6} from one filling of the still. Their method consisted in passing steam, from a copper or tin lined iron boiler thru several traps and finally condensing the steam on cold tubes. The apparatus is fairly simple and the process is a discontinuous one.

Bousfield (18) in 1912 developed two different types of stills One of them was a continuous one giving water with a specific conductivity 0.9×10^{-6}. By the addition of an alkaline permanganate solution to the still he was able to reduce this to 0.75×10^{-6}. His second still is known as the three bottle type. This is charged with good water from the first still and yields water having a specific conductivity 0.5×10^{-6}. The important feature of the first distillation is the condensing of the liquid on cold tubes whose temperatures are regulated. Bousfield experimented with tubes at different temperatures for this condensation and used that temperature which gave a maximum purification. In the three bottle type of still, the middle bottle is used as a trap, the first as a boiler

and the third as a receiving vessel. The operation is carried out under diminished pressure.

In 1913, Robert Bourdillon (19) made some conductivity water with a specific conductivity of 0.086×10^{-6} at 18° C. The principle of his method consisted in washing the vapor of the water with a stream of purified air. The volatile impurities in the vapor were thus swept away from the water and the distillate was collected in a good quality of glass.

In the preparation of conductivity water which is distilled in contact with the atmosphere in a good type of still, the values of the specific conductivity vary from 0.15×10^{-6} to 0.8×10^{-6} mhos. at 18° C. In this laboratory using the general conductivity still, both Williams(20) and Bell (21) have obtained water with a specific conductivity as low as 0.19×10^{-6} at 25° C. Bell by adding phosphoric acid to the first distillate and then subjecting it to a second distillation obtained water having a specific conductivity of 0.17×10^{-6} at 25° C. Millard later obtained water measuring 0.15×10^{-6} without the use of a second still.

The still (22) referred to above is one of 50 liters capacity made of copper and lined thruout with tin. It is heated with a steam coil inside the still. In the upper part of the boiler a trap in the form of baffle plates is attached. The water is collected hotin quartz or resistance glass bottles with a current of steam issuing freely from the bottle. When the specific conductivity of the water reaches as low a value as 0.15×10^{-6}, the variability of its specific conductivity depends much upon the method of the transference of the water from the collecting bottle to the cell. There are stills of the above design at the Massachusetts Institute of

Technology and at the University of Chicago, both of which give water as low as 0.2×10^{-6} at 18° C.

Since the equilibrium between carbon dioxide and water is of such a value as to give a specific conductivity to water of between 0.6×10^{-6} and 0.8×10^{-6} at 18° C, there is no use in attempting to prepare water better than this unless it can be kept constant by keeping it out of contact with the atmosphere. It was deemed wise therefore in the present investigation to make all distillations and dilutions in an atmosphere free from the impurities usually present in ordinary air.

OUTLINE OF THE PROCESS OF PREPARATION OF THE CONDUCTIVITY WATER

The preparation of conductivity water is a process requiring considerable technique and care. Absolute cleanliness in any piece of apparatus coming in contact with the water is necessary. This work was begun in September 1914. It was not until the following fall that any satisfactory results were attained in the work. Altho essentially the same apparatus was at hand then as is now being used, it required about four months before all of the necessary technique could be acquired.

The method, similar to that of R. Bourdillon, consists in heating conductivity water 0.6- 0.8 X 10^{-6} at 18° C in a large quartz flask of about 15 liters capacity, and at the same time passing a stream of carefully purified air, free from carbon dioxide and ammonia through the water which is maintained at a temperature just below its boiling point. If it is assumed that the impurities present in water of the above initial purity consist of carbon dioxide and ammonia they will be removed by the above method. By passing a stream of purified air thru the water just below its boiling point these impurities are slowly removed from the liquid on account of their partial vapor pressure. After the water in the quartz flask has been heated just below its boiling point and the current of air passed thru it for about twenty hours, the cell of three liters capacity, (See Figure II) containing platinum electrodes is attached to the condenser of the still and the distillate, about 2 liters, is collected. The second flask contains electrodes so that the conductivity of the distillate can be measured from time to time. If the first distillate is not satisfactory it is drawn out thru tube (D), attached thru the top and running to the bottom of the cell. The first distillate usually has a specif-

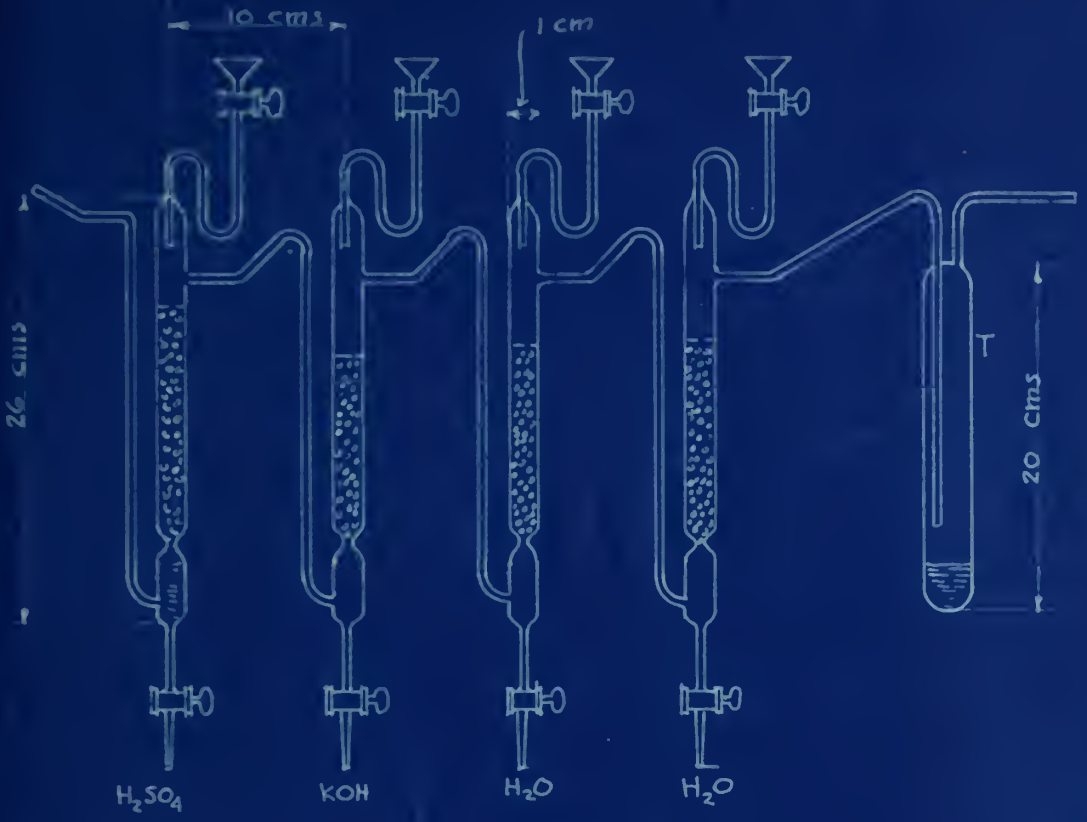


Fig. I

ic conductivity of 0.15- 0.20 X 10^{-6}. If this distillate is removed, the next distillate collected has a specific conductivity of 0.07×10^{-6} at 18° C. This process is continued until finally about 3 liters of water having a specific conductivitybelow 0.065 is obtained in the flask.

DESCRIPTION OF APPARATUS

Apparatus for the Purification of Air

Pure air is obtained by passing outdoor air thru a tower 40 cms. high filled with soda lime, thence thru a train consisting of one tower of dilute sulfuric acid, one of potassium hydroxide, and two of conductivity water. See Figure I. Each tower is filled with glass beads. Following these towers there is a trap (T) to prevent entrainment.

Compressed air from the main supply system is not used because it contains grease, oil and other constituents hard to remove. Pressure is obtained by means of a small Vernon rotary air compressor, which is fed from out doors. The air pressure obtained from this system is very satisfactory for all purposes in the electrical conductivity laboratory.

The Cell

The cell, see Figure II, was made from a round quartz flask of three liters capacity, obtained from the Thermal Syndicate, New York. In order to close the top of the flask and make a support for the electrodes etc., a stopper of Jena Geräte glass was blown and ground into it. As seen from Figure III, this stopper bears four openings, each having a shoulder extending upward to give the supported tube more strength, and an exit tube (X). The following pieces are held

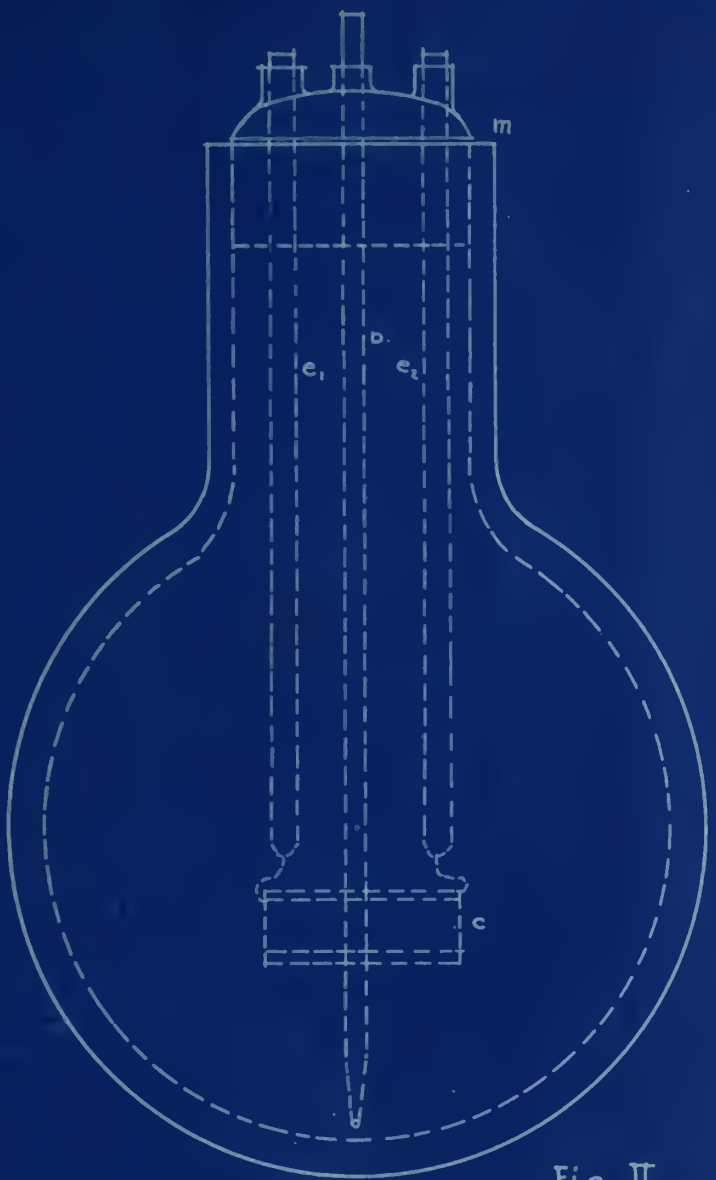


Fig. II

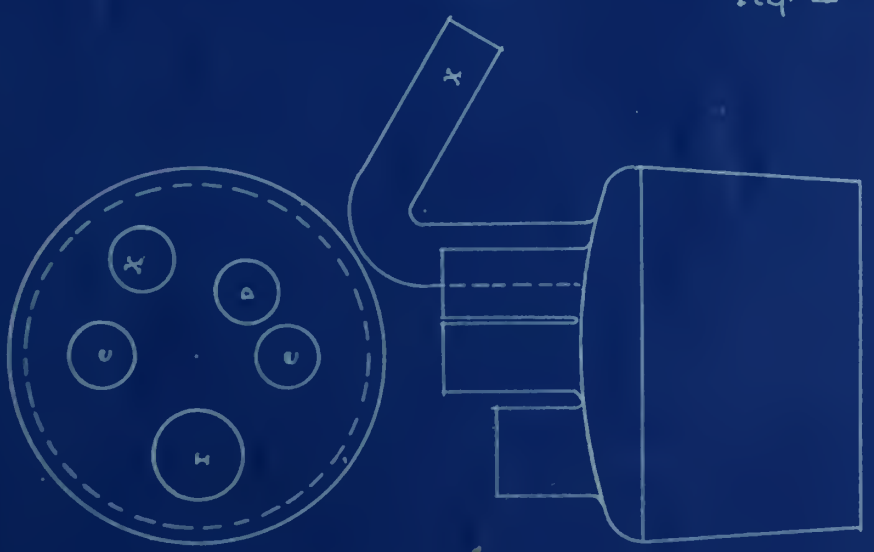


Fig III.

within the cell; The Electrode leads (E), (E') and tube (D), the latter extending to the bottom of the flask for emptying it after the distillations. Opening (I) receives the distillate from the still. All tubes entering the quartz flask are of transparentquartz. These t tubes fit the openings very closely. They are held in place and the joint is made air tight by means of rubber tubing slipped over the shoulder of the opening. The joint between the stopper and the flask is made air tight by means of Stanolax, aliquid paraffin of high purity.

The Electrodes, Figure II, consist of two coaxial platinum cylinders (C), attached to two transparent quartz tubes (E), (E') 0.7 cms. in diameter, 23 cms. long, filled with mercury as leads. The joint between quartz and platinum cylinders was made by means of platinum wire and a special sealing glass. The diameter of the outer cylinder electrode is 2.8 cms. and that of the inner one is 1.7 cms. The distance between them is .55 cms. The length of the electrodes is 2.7 cms. The platinum to quartz seal was made by the Cooper Hewitt Company of Hoboken, New Jersey.

The Distilling Apparatus

The distilling apparatus, see Figure IV, is a quartz flask with a capacity of about thirteen liters. The top(T)is a brass cap 17.5 cms. in diameter, 9.0 cms. in height, fitting down over the neck of the flask inside and outside. This top carries three tubes of block tin, each soldered to the brass cap with block tin. The inside of the cap is also heavily coated with tin. The joint at (Z) is made tight by packing tin-foil in the space between the still and cap and by wrapping a layer of tin-foil around the outside. Over this layer of tin-foil is wrapped some rubberized cloth.

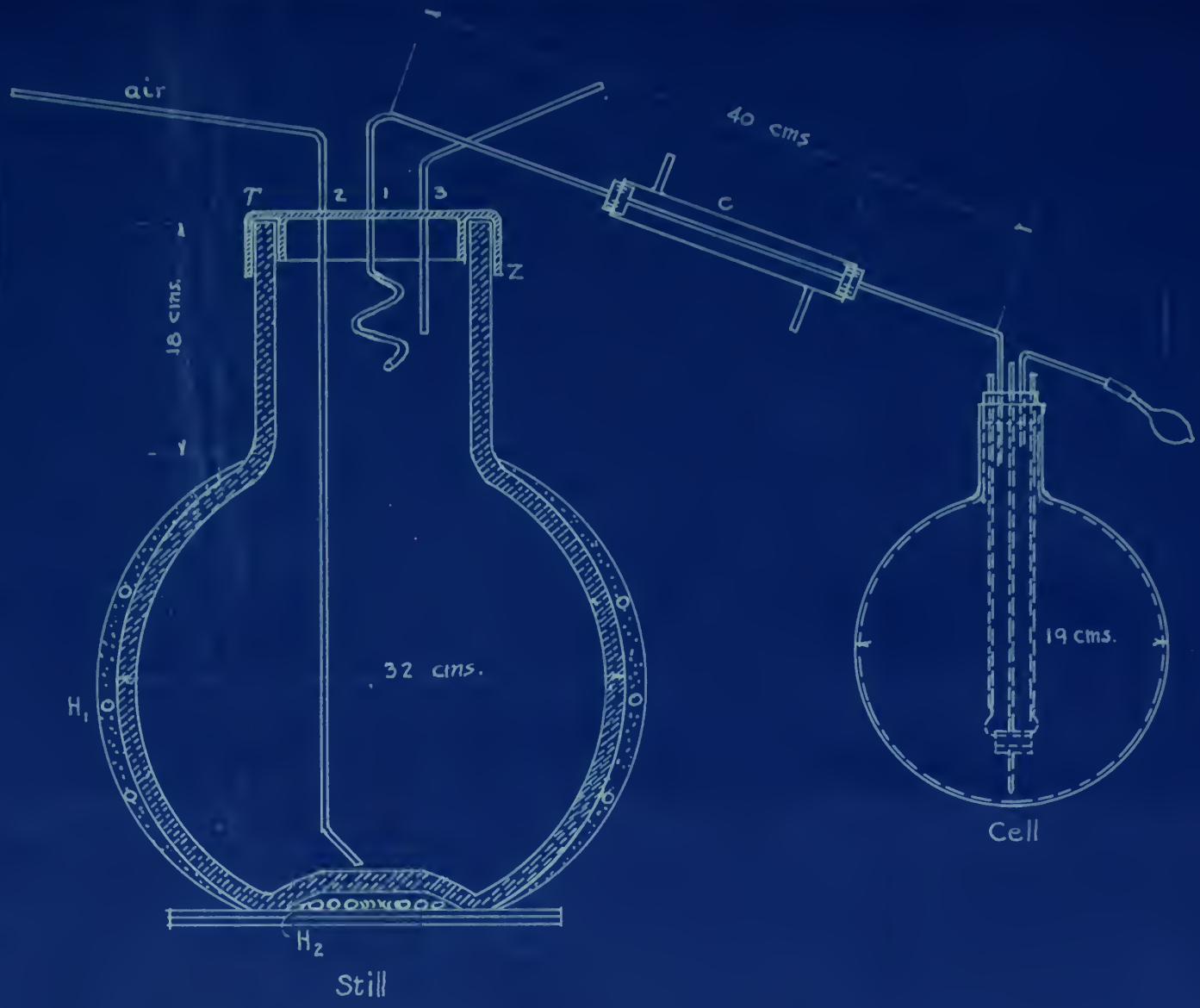


Fig. IV

The tubes coming from the still are as follows; Tube (1) is the distilling tube. Slipped over it there is a glass condenser jacket (C). Tube (2) serves for the admission of the pure air and for filling the still with water. Tube (3) is a short exit tube.

The still is heated electrically on the 110 A.C. circuit. By heating with gas burners no favorable results could be obtained and it was thot that carbon dioxide was passing thru the quartz into the water at spots where local heating was high. The heating element is in two units, (H_1) and (H_2). One unit (H_2) is placed in the hollow in the bottom of still on the outside in series with a rheostat so that the current can be varied between three and five amperes. The other heating unit (H_1) is wrapped around the still below the middle part of the body of the flask. The heating element is of nichrome wire embedded in a plaster of fine asbestos, bone ash and powdered silica. By proper adjustment of these units the regulation of the temperature of the water is secured.

The Constant Temperature Bath

The constant temperature bath, Figure V, is a galvanized iron can, 47 cms. high and 41 cms. in diameter, filled with transformer oil. This oil is dry and is of such a viscosity that it can be stirred as easily as water. The use of oil diminishes the possibility of electrical leaks. The oil is cooled by tap water circulated thru the tube (C). The heater (H) is a coiled nichrome wire wound around a glass tube and the whole placed in a larger glass tube having holes blown in the sides permitting the oil to circulate near the heating unit. The temperature of the bath can be maintained at 18° C ± 0.01 C. The mercury regulator (R) is supported from a ring stand placed so as not to receive the jars of the stirring mechanism.

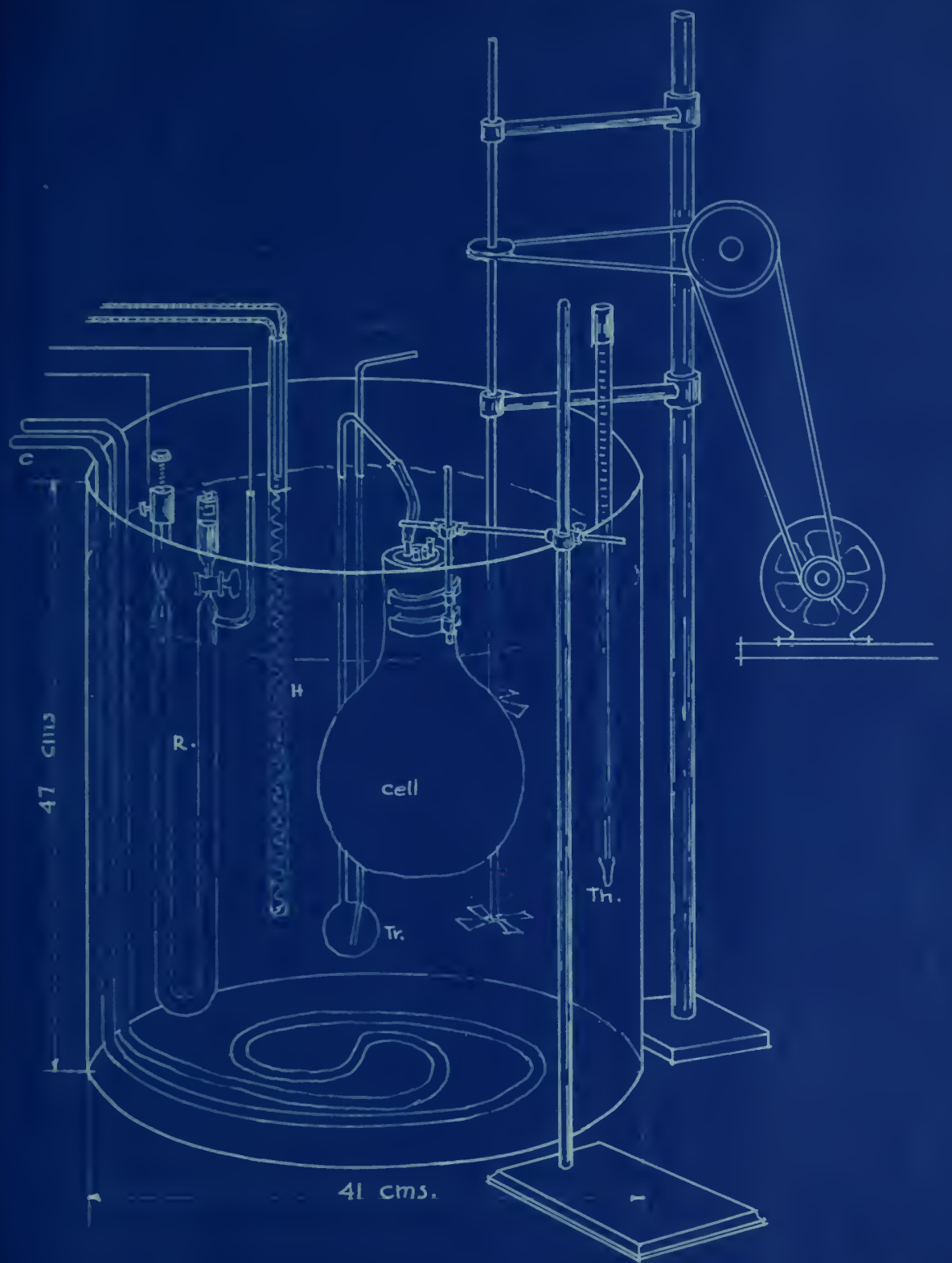


Fig. V

Shunted around the leads of the regulator there is a tin-foil condenser. By this method no trouble is caused by excessive sparking and subsequent formation of a scum on the surface of the mercury. Purified air is passed thru a trap, (Tr.) containing a small quantity of conductivity water before it is sent thru the cell. This trap is submerged in the bath and brings the air to the proper temperature so that it will not effect the temperature of the cell contents. Passing air thru the cell also enables the water to come to the temperature of the bath very quickly. In the case of solutions this current of air also serves to agitate the solution in such a way that it is thoroughly mixed.

The Electrical Measuring Apparatus

The measuring apparatus is that described by Washburn and Parker (23) . It consists of a high frequency generator, milliammeter, special duplex condenser, frequency meter, special Kohlrausch bridge, Curtis Coil Resistance Box, small variable air condenser etc.

The High Frequency Generator was manufactured by the Siemens Halske Co. It has a normal frequency of a 1000 cycles but any desired frequency between 450-1800 cycles can be obtained by the regulating of the speed. The instrument is mounted in an adjoining room on a double felt pad, then covered with an inverted box lined also with a double layer of felt. By this method of shielding the sound of the running machine is lessened to a minimumm. A test description of this machine and the quality of the sine wave is given in Catalog # 48 page 10 Leeds and Northrup.

The Bridges

Two types of bridges have been used in this investigation. One of them for measuring high resistances, the other for low

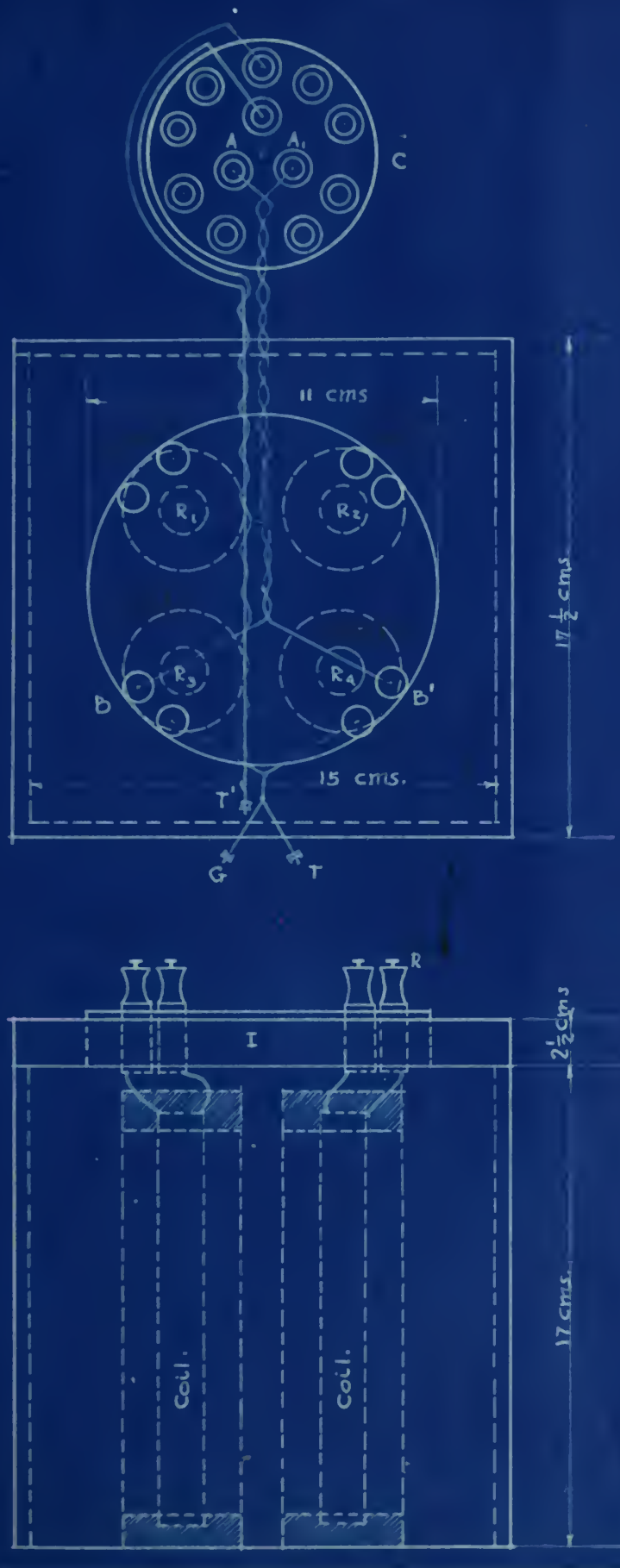

A
A1
C
11 cms
R1
R2
R3
R4
B
B'
15 cms.
17½ cms
T'
G
T
R
I
2½ cms
17 cms.
Coil.
Coil.

Fig. VII

resistances. In the design of a bridge it is aimed to have all the arms of the bridge equal, for under that condition measurements attain a maximum accuracy. The resistance (R_B) of the slide wire and the extension coils should be so chosen that it accords with the following equation, Washburn (24).

$$R_B = 2\sqrt{R(R_B + 2R_T)}$$

where R = resistance of the cell or resistance box.

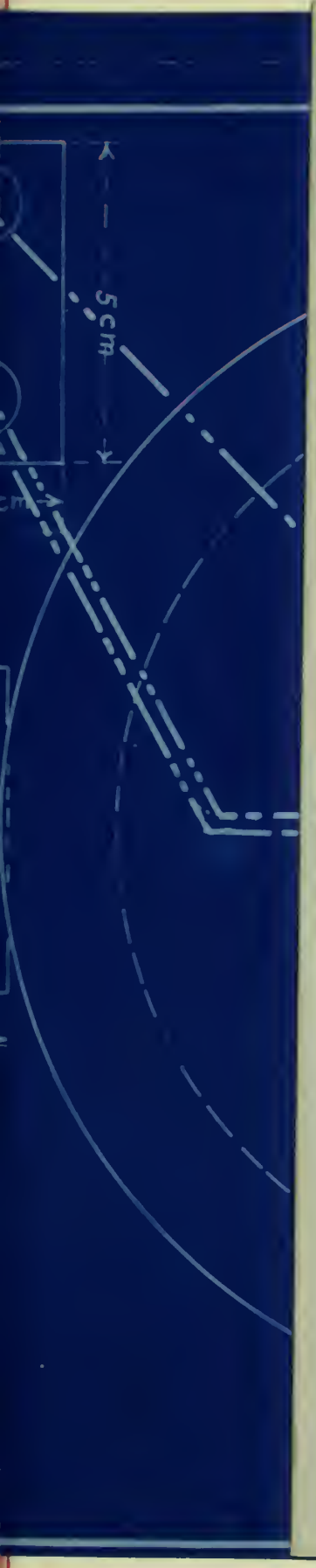
R_T = " " " telephone.

However since "except for very small or very large values of(R)it is not necessary to pay much attention to fulfilling the condition expressed by this equation" only two bridges have been used , one having a resistance of 12000 ohms, the other a resistance of 250 ohms.

The Constant Ratio Bridge

This bridge, Figure VII, is the one used for the measurement of the high resistances, i.e, the resistance of the water. It consists of four Curtis Coils mounted in a square mahogany box. The coils are set in glass cylinders with blocks of ceresine, shaded in the diagram, as supports on either end. This enclosure in the cylinders is air tight thus keeping the moisture content within constant. The bottom of the box and the insert (I) in the top carrying the connectors (R) are of specially prepared wood, impregnated with ceresine. The Commutator (C) is used in connection with this bridge. The coils are of the following units in ohms, 2-1000, 1-3000, 1-10000. By means of these coils several ratios are possible.

The current is brought in at A and A' from beneath the commutator. It is thrown from there directly on to the ends of the bridge(B) and (B'). The point (G)is connected to the earth, the point (T) to one end of the telephone. By means of this bridge the resis-

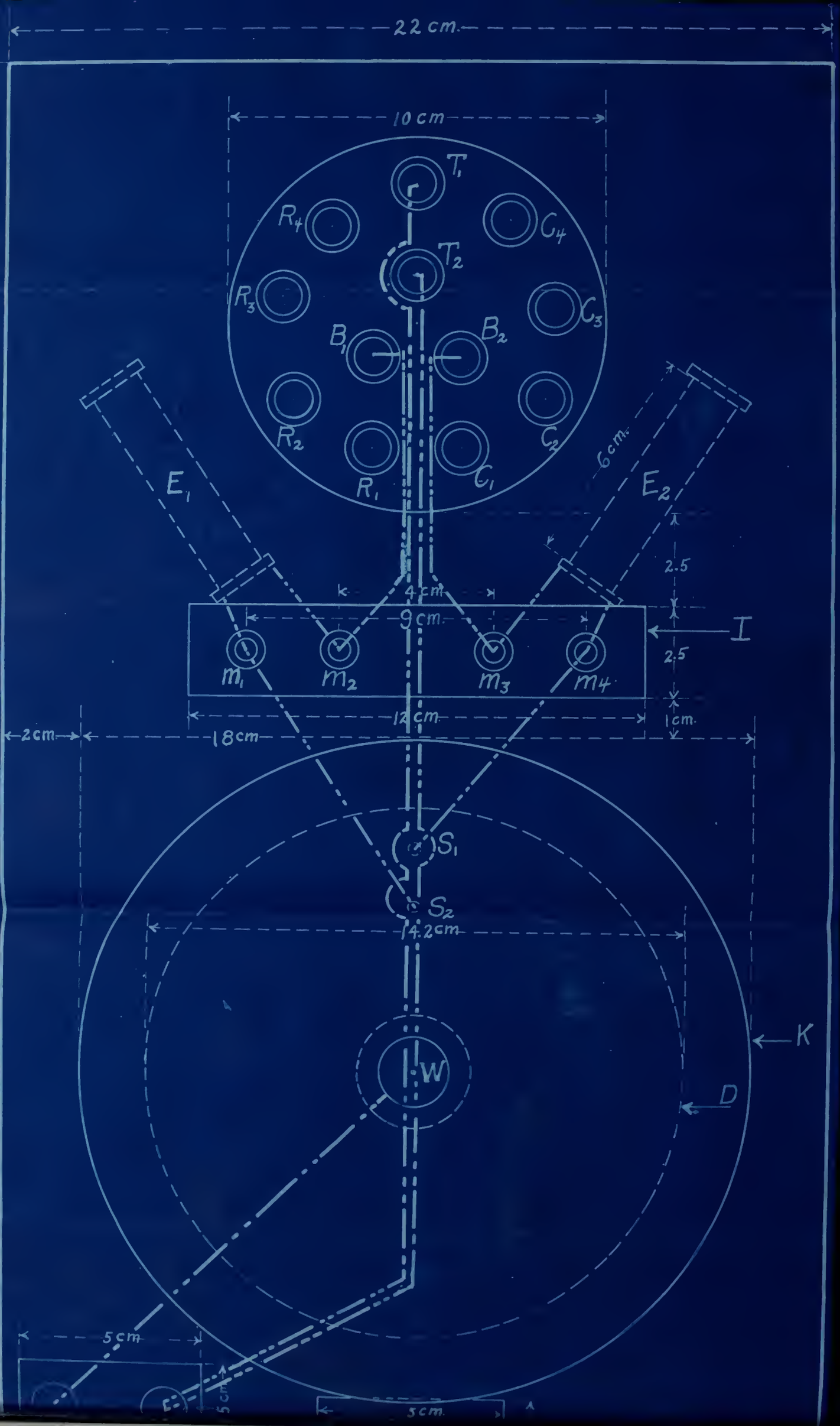


a precision of

nce of the dilute
in Figure VI. The
wound around a
n coils (E_1) and
ntral portion of
tance Wire *. The
resistance of 873
.s is # 35 (B&S) and
ıds of the central
extension coils
) (m_4) at (B_1) and
oximately 250 ohms.
n is divided into
to 1/20th. The
tely 1/20th of the

P_1) and (P_2). (P_1)
(W). (P_2) is con-
or by two wires of
) and (P_2) are sunk

ns of wood holding
m_2), (m_3), (m_4) are
mmted with ceresine.
914. Page 40.


22 cm.
10 cm
T1
T2
R4
C4
R3
C3
B1
B2
R2
C2
R1
C1
E1
E2
6 cm.
2.5
4 cm.
9 cm.
I
2.5
m1
m2
m3
m4
12 cm.
1 cm.
2 cm.
18 cm.
38 cm.
S1
S2
14.2 cm
K
W
D
5 cm
5 cm.

tance of the water, 450000 ohms is measured with a precision of 0.1 % .

The Kohlrausch Bridge

This bridge is used to measure the resistance of the dilute solutions. A sketch of the wiring design is shown in Figure VI. The bridge consists essentially of the central portion wound around a circular block of ceresined wood (D), the extension coils (E_1) and (E_2) and the commutator. The wire used on the central portion of the bridge and the extension coils is Therlo Resistance Wire *. The part wound around the drum is # 25 (B&S) and has a resistance of 873 ohms per 1000 feet, the part in the extension coils is # 35 (B&S) and has a resistance 8,917 ohms per 1000 feet. The ends of the central wire are at (S_1) and (S_2) or more exactly when the extension coils are " cut out" by joining (m_1) to (m_2) and (m_3) to (m_4) at (B_1) and (B_2). The total resistance of the bridge is approximately 250 ohms. The portion of the bridge wound on the wooden drum is divided into 1000 equal parts. Each division can be estimated to 1/20th. The "center of the bridge" has a resistance approximately 1/20th of the total length of the bridge.

The telephone is attached to connectors (P_1) and (P_2). (P_1) is connected to the sliding contact indicated by (W). (P_2) is connected to the cups, (T_1) and (T_2) in the commutator by two wires of equal length and resistance. The connectors (P_1) and (P_2) are sunk into a block of ceresined wood.

The drum (D), the commutator and the blocks of wood holding the connectors (P_1) and (P_2) and the cups (m_1), (m_2), (m_3), (m_4) are made of specially prepared wood, bass wood impregnated with ceresine.

* Driver Harris Wire Co. Catalog L. April 1914. Page 40.

Surface spaces between wiring are covered with ceresine to prevent surface leaks.

In the commutator are sunk a number of holes into which brass cups (R_1), (R_2), (C_1), (C_2), etc. are inserted. These can be connected by cross wires to cups (B_1), (B_2), (T_1), (T_2). To (C_3) and (C_4) are connected the leads to the cell, to (R_3) and (R_4) are connected the leads to the resistance box. The current enters at (B_1) and (B_2) from below the commutator.

The precision of the bridge is 1 part in 400,000 parts, when the resistance of (X) is 10,000 ohms. For a fuller description of the details of these bridges and the theory of their design, see Washburn (25).

The Resistance Box

The resistance box is a Leeds Northrup type made up with Curtis coils. There are five dials of the following units: 10000, 1000, 100, 10, 1,. Values of these coils were checked by the U. S. Bureau of Standards at Washington.

The Sound Proof Booth

In order to get a good setting upon the bridge there must be perfect quiet in the vicinity of the telephone receiver. Since it is necessary to have the frequency machine close at hand for control purposes etc. and since a little noise is made even with the best shielding, a sound proof booth is used in which to take the resistance readings. The booth is a double walled telephone booth, 2.3 meters long, 2.9 meters high, and 2.4 meters deep. Inside on the rear wall there is a switch board panel. A plan of the switch board is shown in Figure VIII. Fitting over the board there is a galvanized iron box having a drop front to it. This box is grounded and

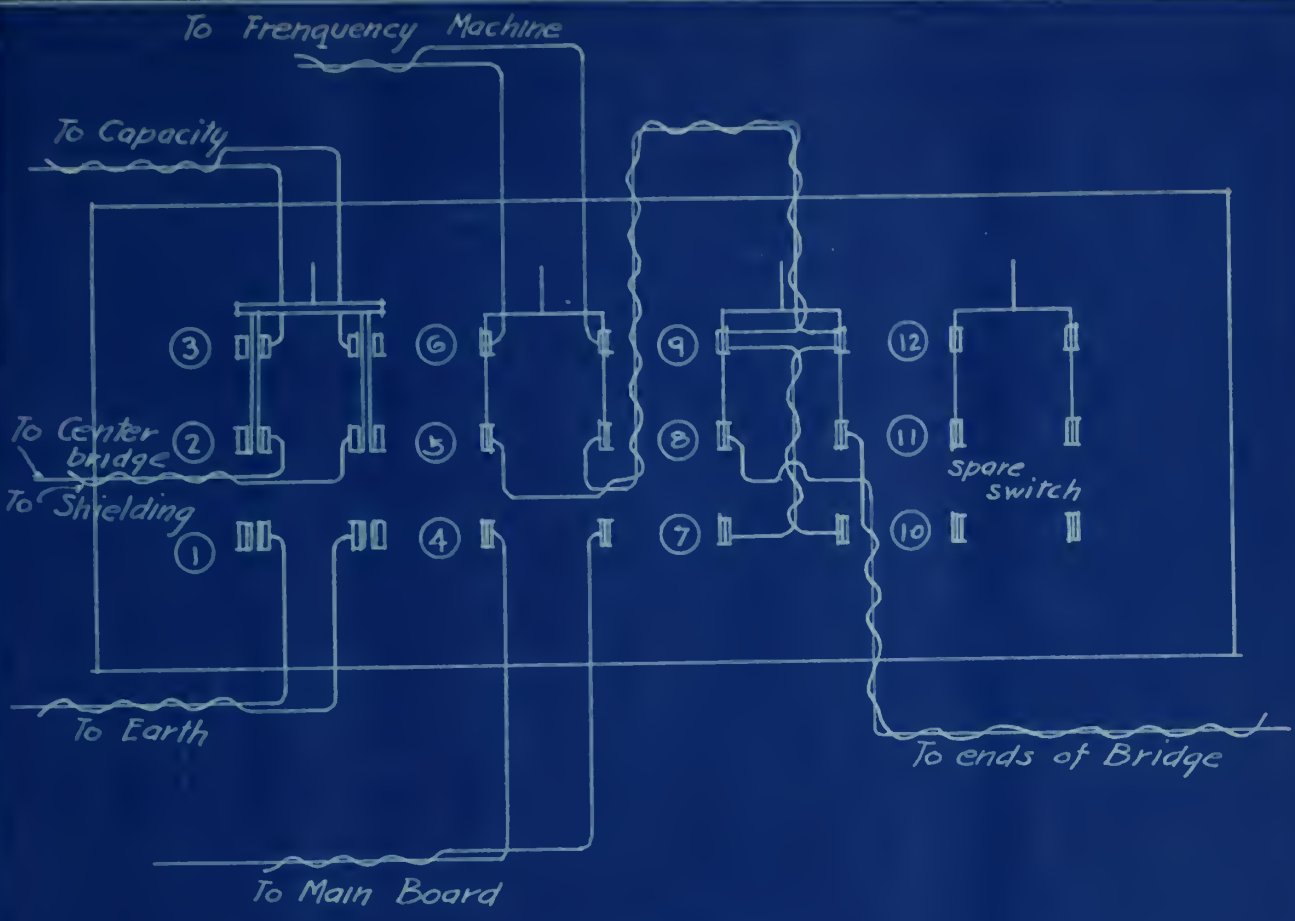

To Frenquency Machine
To Capacity
3
6
9
12
To Center bridge
2
5
8
11
spare switch
To Shielding
1
4
7
10
To Earth
To ends of Bridge
To Main Board

Fig. VIII

acts as a shield to keep the varying electro magnetic field off the instruments.

A shelf 45. cms. wide, 75 cms. above the floor runs across the back and one end. This shelf is used to set the bridges and the other electrical measuring instruments upon. The equipment of the booth also contains a D.C. circuit to a light and to a D. C. fan. A good isolation from noise is afforded by this booth. With the machine running at its normal speed there is only the faintest sound in the booth.

The arrangement of the board, Figure VIII, is such that the shielding and the "center of the bridge" can be grounded either to the earth or to a variable capacity by the throwing of switch # 2 to # 1 or # 3 respectively. By a proper adjustment of switches # 5 and # 8, an alternating current or a direct current can be thrown upon the ends of the bridge # 8. The movement of switch # 8 from # 7 to # 9 reverses the current, for # 7 and # 9 are each connected in a reversed way to switch # 5.

The switch board is connected up as follows:

1. Capacity to earth.
2. Connected to center of bridge and to parts that are shielded.
3. Large variable capacity.
4. Distribution board in the department.
5. Connected to # 7 and # 9.
6. Exposed circuit running to machine in the adjoining room.
7. To # 5.
8. Connected to the ends of the bridge.
9. To # 5.

METHODS OF CLEANING THE CONTAINING APPARATUS FOR WATER AND SOLUTIONS

All pieces of apparatus coming in contact with the water must be perfectly clean. The flasks etc. are washed very thoroughly with conductivity water 0.6×10^{-6} to release any material clinging or absorbed on their surfaces. Later they are "steamed out". This is done by leading steam obtained from heating a large Jena flask, 4 liters capacity, filled with conductivity water 3.6×10^{-6} into the cell and from there it flows back into the flask. The Jena flask is heated electrically and hence the steaming can be carried out safely by letting the flask boil continuously.

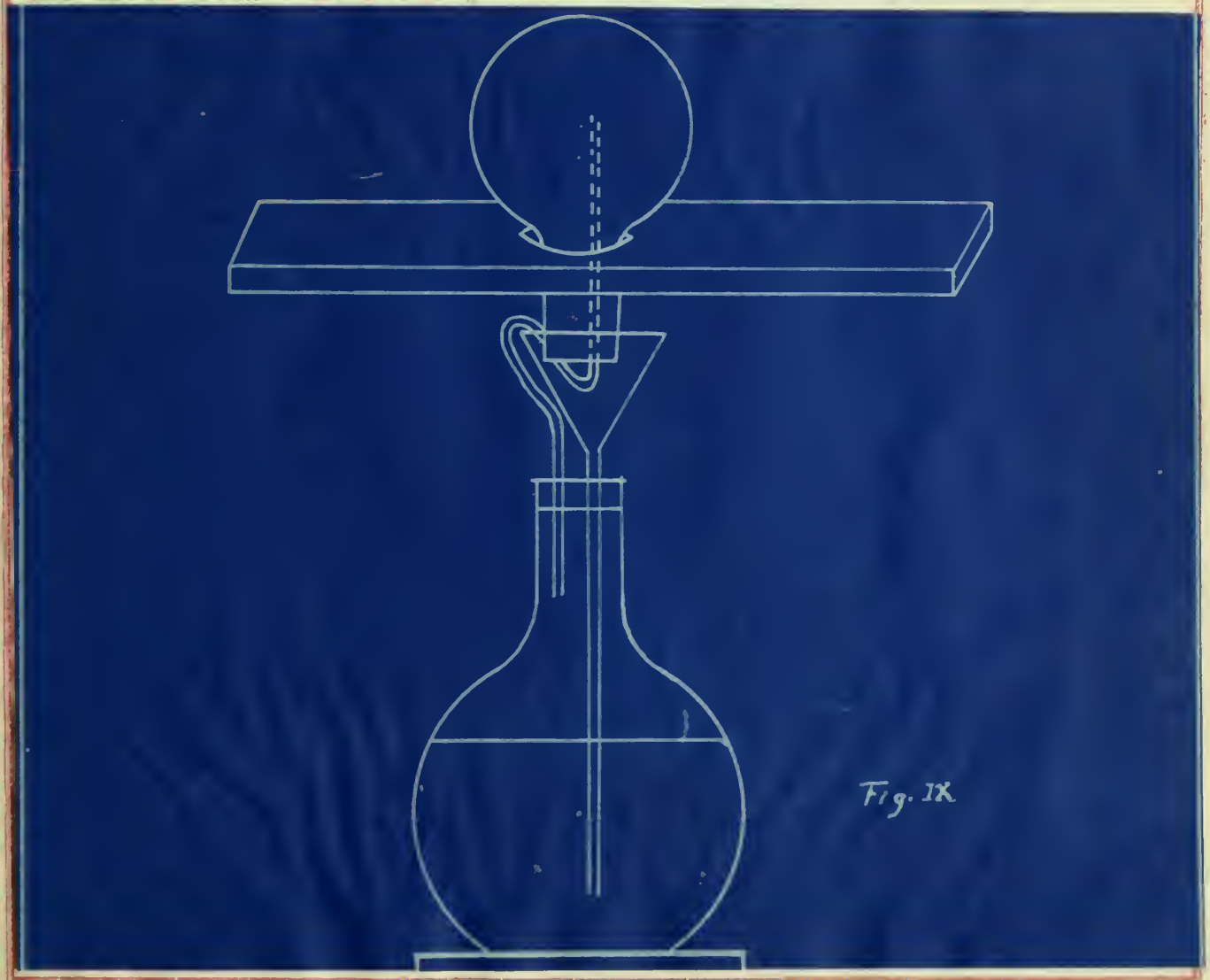


Fig. IX

The electrode is rather hard to clean. Since at the more concentrated dilutions when the salt is measured, the solution has a normality of 0.0015 - 0.001, there is the necessity of covering the electrode with platinum black. The electrode must therefore be cleaned a couple of days with good water in order to remove the adsorbed electrolyte. This is accomplished by first washing the electrode thoroughly with good water to wash away the bulk of the material clinging to it, then it is placed in an apparatus similar to a Soxhlet Extractor, Figure X. Clean steam is led into the vessel from below. This is partially condensed and the electrode is continually agitated by the movement of the steam bubbles. If the flask is heated at a slow rate the apparatus automatically empties itself at regular intervals, and a continual supply of clean water is in contact with the electrode. By this method the electrode can be cleaned in two days.

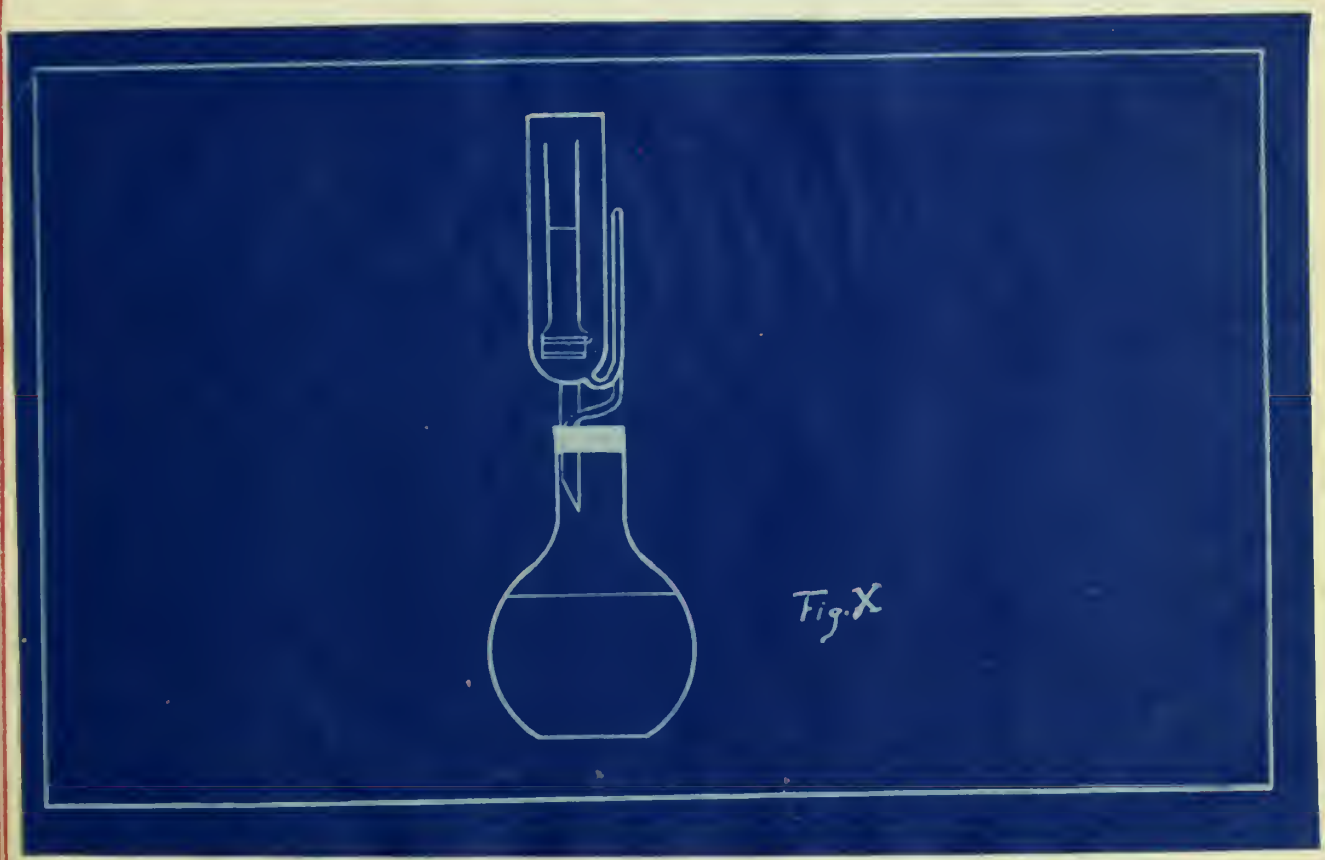


Fig. X

METHODS OF PROCEDURE

After all the apparatus has been cleaned, there is prepared in the general conductivity still about twenty liters of conductivity water with a specific conductivity below 0.4×10^{-6}. The collection is made in special resistance glass bottles. This water also will not be siphoned off into the large quartz still. After the still is filled with this water, one unit of the electric heater is turned on and the water gradually heated. The water is not boiled but heated to a point below boiling so that only a small amount is lost by distillation. At the same time the purified air is turned on and the removal of the carbon dioxide begins. This process of heating and driving off the impurities is continued about 36 hours. Before attaching the cell to the still both heating units are turned on and the atmosphere over the boiling liquid is well swept out. The electrode cell is now attached to the still in such a way that no external polluted air is allowed to get inside the cell. This is done by having a stream of purified air sweep out the opening into which the condenser tube fits.

With the cell attached to the still in such a way as to isolate the contents of the system from the atmosphere, the distillation is begun by starting the second heating unit. The first two or three hundred cubic centimeter portions are removed here tube (D) in such a way as to allow the air coming through the still to replace the water removed. When the cell is filled to a height well above the electrodes, with the distillation still going on, a preliminary measurement of the resistance is made. Assuming the temperature of the water to be that of the room, the measurement is corrected to 18° C to ascertain whether the water collected is of the desired

purity. Should the water possess a conductance greater than that desired it is removed by the same method as the small portions at the beginning of the distillation are removed. A second distillation without detaching the cell is then begun and when the filling is complete, another measurement is taken. Since the large flask will distill over enough water to fill the cell three times the water can be drawn out once more if necessary. It is sometimes necessary to obtain the final water from the third portion but unless something is radically wrong in the system at least one cell of good water can be obtained from a single filling of the large quartz still.

When the water is collected the cell must be detached from the still in such a way as to exclude atmospheric air. This is done by passing a slow current of purified air back through tube (D) as the break is made. After the break is made a rubber stopper covered with clean tin foil is inserted into the left opening in the glass stopper. The cell is then removed to the constant temperature bath where purified air is led into tube (D) and passes out tube (A). By means of this passage of air the water is agitated so that it comes to the temperature of the bath quickly. The positive pressure on the inside also acts as a barrier to any polluting air that may otherwise enter the cell through defective joints.

RESULTS

The first encouraging results were obtained October 7, 1915. The distillation was started at midnight October 6, and continued until 8 o'clock next morning. The water of first distillation measured at 25° (temperature of room) was 0.208 X 10^{-6}. This water was drawn out through tube (D) in a way already described. The second distillation was started at 10 A. M., October 7 and stopped at 4 P.M. The air was being blown through the apparatus both from the still, and from the cell end through tube (D). The conductance fell to 0.076 X 10^{-6} at 25° C., temperature of the room. The conductivity of the water remained constant while air was being passed through it from the large flask for 30 hours. The water was then allowed to stand in the flask with the air pressure off. In 30 hours the conductance rose to 0.300 X 10^{-6}. The flask was then disconnected from the still and purified air was blown through tube (D) and out the soda-lime tube.

TABLE IV

Temperature of Room	Time	Specific Conductivity. $\times 10^{-6}$
25° C	0	.358
24.9	38 minutes	.292
24.8	1 hr. 10 min.	.202
24.6	2 hr. 40 min.	.140
25.0	6 hrs. 10 min.	.063

The above experiment shows quite clearly the necessity of keeping the external air from contact with the water. The impurities however can be removed if the purified air is passed through the water again.

This quality of water has been prepared repeatedly for the past year and one half. A few of the samples at 18° C are given below.

TABLE V

Date	Specific Conductivity. mhos. X 10^{-6}
Dec. 28, 1915.	0.0575
Jan. 15, 1916.	0.0590
Mar. 18, 1916.	0.0625
Feb. 2, 1917.	0.0665
Feb. 19, 1917.	0.0610
Feb. 24, 1917.	0.0633
Mar. 6, 1917.	0.0533

Water of low specific conductivity can be kept in the quartz cell, practically unchanged, provided the purified air is passed thru it continually. The water has been preserved constant over periods as long as twelve hours. Experiments were made to determine if any pollution of the water was caused by with-drawing the cork from the opening (I) for thirty seconds, then replacing it. No change in the conductivity of the water was noticed in these experiments. In measuring the conductivity of the dilute solutions an entire series in some cases was run in less than two hours. It is reasonable to believe that the conductivity of the water remained constant over each individual series.

III

THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF DILUTE SOLUTIONS OF POTASSIUM CHLORIDE

THE MEASUREMENT OF THE ELECTRICAL CONDUCTANCE OF DILUTE SOLUTIONS OF POTASSIUM CHLORIDE AT 18° C

Probably the most accurate electrical conductivity measurements on dilute potassium chloride solutions are those made by Kohlrausch and Maltby (26). Whetham and Paine (27) and Paine and Evans (28) have studied very carefully the conductivities of some dilute acid and alkali solutions. The latter studies were made chiefly to investigate the problem of "water correction" in these dilute solutions.

On account of the relatively high specific conductivity of the water used in the experiments of Kohlrausch and Maltby, the values of the equivalent conductances are questionable in the dilute solutions. Their results for potassium chloride at 18° C. for dilutions greater than 0.001 N have even been challenged by Kraus and Bray (29) who find that their general dissociation formula does not correspond to Kohlrausch and Maltby's experimental values in dilute solutions.

Because of the unreliability of the present data in the dilute solutions, the measurement of the conductivity of potassium chloride was repeated by the writer. A repetition of these measurements upon solutions made up with a better conductivity water meets the objection of Kraus and Bray to the older data. The water used by Kohlrausch and Maltby in their measurements of potassium chloride had a specific conductivity of 0.92-0.96 X 10^{-6} at 18° C. The water used in the present investigation had a specific conductivity of 0.053 -0.074X10^{-6} reciprocal ohms at 18° C, or about 15 times better than that used by Kohlrausch and Maltby. A comparison of the magnitudes of the results-

ing corrections due to water of these respective conductivities has already been referred to. Table III.

EXPERIMENTAL

Preparation of the solutions

The preparation of the water has been described in Part I of this investigation. The potassium chloride was prepared by further purifying Kahlbaum's best product. This purification consisted in re-crystallizing three times from conductivity water, partially drying it by centrifuging, then fusing it in platinum. It was stored for use in small weighing bottles over small calcium chloride in a dessicator.

The procedure for making up the final solutions required some preliminary study. They were first made up by adding a weighed amount (1 c.c.) of a dilute solution, about 0.005 N, to the water contained in the cell, by means of a small weighing pipette. By this method of dilution it was thot that any desired concentration could be obtained. However for some reason the Λ_c values measured by this method reached a maximum. This was caused probably by the fact that all the solution did not reach the water and hence produced low results. This condition was possible because one could not see in the case of the last drop off the pipette where it fell, into the water, on the side of the flask, or onto the leads, due to the opacity of the quartz flask.

Another method, attempted, was to introduce into the cell with the aid of a small platinum pail, 19 mm. deep, holding about 0.7 c.c., the salt contained in a weighed amount of a dilute solution. In order to eliminate a possible correction for the water contained in the solution, the water was first removed from the salt by evap-

oration in a calcium chloride desiccator, the potassium chloride remaining as a residue. The entire pail was then dropped in to the cell containing the conductivity water. The low Λ_c values obtained in this way led us to believe that the salt was not diffusing out of the pail

The method finally adopted was merely the dropping of a small crystal, 5.0 milligrams, into the water in the cell. The crystal was weighed out on a small platinum pan then transferred carefully to a shallow platinum bucket. This bucket was made by folding platinum foil and attaching to it small wire supports. The salt crystal and bucket were then dropped into the water. Merely dropping the crystal alone does not assure its reaching the water without its hitting the inside of the neck of the flask or the leads. Small pieces of platinum, cleaned and dropped into the water as above, did not change the conductivity of the water. This method of making up the solutions is limited because of the difficulty of weighing, at the required accuracy, crystals small enough to give the proper dilution.

Apparatus

The balance used for the weighing was an assay balance of a guaranteed sensibility of 0.005 milligrams with a load of one gram. It showed a sensibility of 0.001 milligrams with a load of 20 milligrams. The weights used had been previously calibrated at the U. S. Bureau of Standards at Washington.

The cell and constant temperature bath have been previously described. In the measurement of the resistance of the water the constant ratio coil bridge was used. The Kohlrausch bridge was used

in the measurement of the resistance of the solutions.

The bridge wire was calibrated only at those points (P_1), and (P_2) where it was desired to know the ratio of the arms of the bridge in the measurement of the solutions when the bridge readings were (P_1), and (P_2). This was done by substituting in the bridge arms in place of the cell and known resistance,two adjustable Curtis coil resistances (10000 ohms) and then adjusting one of them till a silence in the telephone was reached when the bridge was set at the point (P) in question. The resistance of these coils was then corrected and the ratio between the corrected resistances was used as the ratio of the arms of the bridge when the setting was at the point (P).

Determination of the Cell Constant

The cell constant was obtained by comparing the resistance of a solution in the cell with the resistance of the same solution in a second cell of known cell constant. The comparison solution was one of potassium chloride about 0.001 N made up with conductivity water in equilibrium with the carbon dioxide of the air.

The cell with the known cell constant was measuredby Clark in this laboratory in 1915 at 0° & 25°C and checked by myself in 1916 at 25 C to within 0.01 % of the formers value. This constant was found by the use of the 0.1 N solution of potassium chloride as described by Kohlrausch (30). The value of the cell at 18° C, found by interpolating between 0°C.& 25°C. is 0.6040

Table No. VI

Date	Resistance in unknown cell	Resistance in known cell	Cell Constant
Feb. 26.	146.443	3631.62	.024356
March 6.	134.366	3333.23	.024348
March 16.	118.222	2932.22	.024352

Density of the Solutions

The densities of the solutions were the densities obtained from the data of Lamb and Lee (31). The relative densities were given by them at 20.004° C, compared with water at the same temperature. To refer those densities to the absolute system at 18° C, they were multiplied by 0.998622, the absolute density of water at 18° C.

Table No. VII

Moles per liter	Lamb Water at 20.004°-1 relative density	Lamb X.998622
.0001	1.0000048	998626
.0002	1.0000097	998632
.0005	1.0000242	998646
.001	1.0000485	998670
.002	1.0000971	998719
.005	1.0002426	998864

RESULTS

The equivalent conductances of potassium chloride given below are at 18° C ± 0.01., The molecular weight of potassium chloride used in the calculation was 74.56. All weights were corrected to vacuo.

Table VIII

January 24, 1917. Water $= .07404 \times 10^{-6}$

Moles per Liter $\times 10^6$	Specific Conductivity $\times 10^6$ corrected	Equivalent Conductance
23.958	3.10226	129.490
46.129	5.96758	129.368
81.343	10.5047	129.141
119.574	15.41763	128.938
183.019	23.558	128.720

Table IX

February 2, 1917. Water $= .06645 \times 10^{-6}$

Moles per Liter $\times 10^6$	Specific Conductivity $\times 10^6$ corrected	Equivalent Conductance
7.4945	.968807	129.268
26.467	3.42878	129.547
42.251	5.46522	129.351
74.563	9.62983	129.149
102.58	13.2337	129.005

Table X

February 10, 1917. Water=. 06998 X 10^{-6}

Moles per Liter X 10^6	Specific Conductivity X 10^6 corrected	Equivalent Conductance
23.821	3.08509	129.513
58.647	7.58402	129.315
103.837	13.4033	129.08

Table XI

February 24, 1917. Water=.06330 X 10^{-6}

Moles per Liter X 10^6	Specific Conductivity X 10^6 corrected	Equivalent Conductance
31.951	4.13537	129.430
61.994	8.00763	129.166
123.36	15.9024	128.911

Table XII

March 6, 1917. Water=.05335 X 10^{-6}

Moles per Liter X 10^6	Specific Conductivity X 10^6 corrected	Equivalent Conductance
26.960	3.48776	129.369
60.878	7.86092	129.125
104.17	13.4308	128.926
154.14	19.8425	128.733
236.09	30.3397	128.510

IV

ADSORPTION

ADSORPTION

In ascertaining the concentration of dilute solutions adsorption phenomena must be considered. In the case of quartz, Briggs (32) has measured the adsorption of the hydroxides and carbonates of several metals and finds a positive adsorption. He reports also that the chlorides of potassium, sodium and ammonium fail to show any measurable adsorption either by titration or by conductivity methods. The accuracy of his experiments is not stated and therefore no exact conclusion can be deduced. Kohlrausch (33) has considered the possibility of electrode adsorption with neutral salts and reports that platinum appears to be free from such effects.

Experiments were therefore made by the writer with quartz and potassium chloride in order to determine the extent of the adsorption or at least its upper limit. This was accomplished by the following conductivity method. The specific conductivity of the solution.001 N- .0008 N, was first measured and then a definite quantity of well cleaned quartz fragments was dropped into the solution, and the specific conductivity again determined.

Preparation of the Quartz fragments

The quartz fragments were prepared from pieces of broken quartz apparatus. These were first broken up into small pieces and then ground up in a ball mill. The resulting quartz powder was then washed with conductivity water until the wash water showed no increase in conductivity. The fragments were next dried in a quartz flask and finally heated to about 300°C to drive out the last traces of water.

A blank run was made by adding a definite amount of the prepared quartz to conductivity water. The resulting change in the conductivity of the water can be seen in Table XIV. This change in conductivity is equivalent to the change produced by the addition of 2.26×10^{-7} equivalents of potassium chloride to the solution. The result of only one of these experiments, the one showing the greater pollution, has been calculated. This change in terms of concentration of potassium chloride is used as the polluting effect upon the solution when the quartz is added to it.

Determination of surface of quartz

The surface of the quartz was determined as follows: The entire amount was separated into fractions by means of sieves. The weight of each fraction was noted. The average diameter of the particles in each fraction was measured by means of a microscope having an eyepiece calibrated to a grating spaced to hundredths of a millimeter. In the calculations of the surface of the particles, they were assumed to be perfect spheres, an erroneous assumption for the quartz fractured into irregular pieces.

The surface of any fraction may be found from the following data: The average diameter of the particle, the weight of the fraction and the specific gravity of quartz, 2.21 . An example is given below for the quartz left on sieve No. 40 . Also see Table XIII.

$$(\text{Diameter})^3 \times \pi/6 = \text{Volume}$$
$$(.2821)^3 \times \pi/6 = 1.175 \times 10^{-2} \text{ cu. mm.}$$

$$\text{Volume} \times \text{weight of 1 cubic mm.} = \text{weight of particle.}$$
$$(1.175 \times 10^{-2}) \times .00221 = 2.597 \times 10^{-5} \text{ grams.}$$

$$\frac{\text{Weight of fraction}}{\text{Weight of particle}} = \text{number of particles in fraction.}$$

$$\frac{1.25}{2.597 \times 10^{-5}} = 4.813 \times 10^{4}$$

$(\text{radius})^2 \times 4\pi$ = average surface of particle.

$\left(\frac{.2821}{2}\right)^2 \times 4\pi = 0.2498$ sq. mm.

Surface of particle X Number of particles = Total surface of fraction.

$.2498 \times 4.813 \times 10^{4} = 1.202 \times 10^{4}$ sq. mm.

Table XIII

Sieve, meshes per inch	Average diameter millimeters	Total surface of Fraction Sq. Cms. ____ X 10^{-3}	Weight of Fraction grams.
40	0.282	.120	1.25
60	0.246	.678	6.15
80	0.149	2.405	13.20
100	0.0968	2.425	8.65
120	0.07214	1.200	3.19
200	0.5832	3.029	6.51
over200	0.3197	7.037	8.29
TOTAL		16.894	47.24

The quartz was thus found to have a total surface of 347.0 Sq. Cms. per gram.

METHOD OF EXPERIMENTATION

The cell consisted of a small quartz flask, 250 c.c. capacity and a dipping electrode, Figure XI.

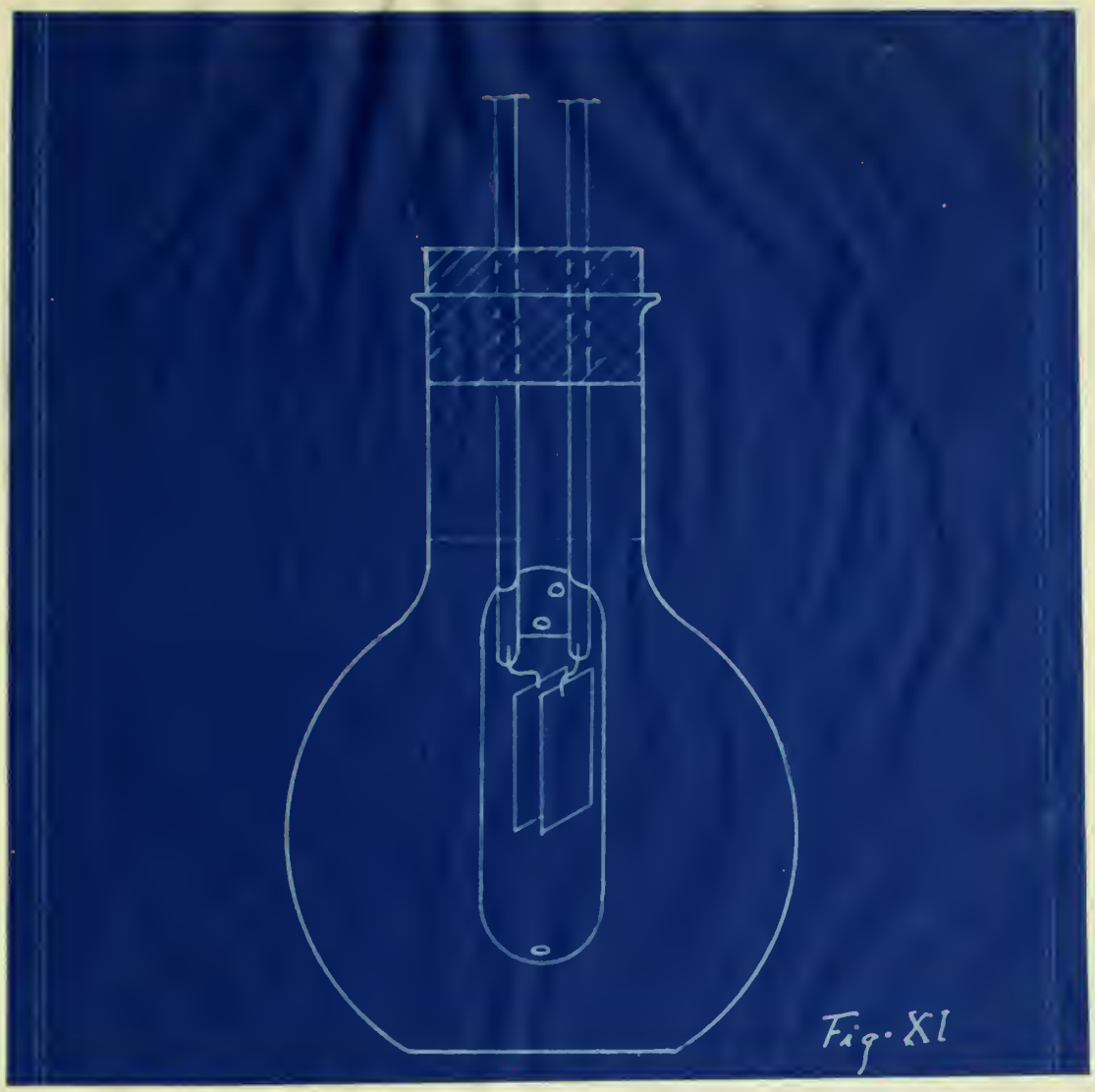


Fig. XI

The cell was filled with conductivity water and allowed to come to the temperature of the bath. The specific conductivity of the water was measured. A small crystal of potassium chloride was then dropped into the water and the specific conductivity of the solution measured. As soon as the conductivity became constant, the cleaned quartz was dropped into it and the conductivity again noted.

The concentration of the solution was determined from its conductivity, using the Bates equation and the constants for potassium chloride. The values found are given in Table XIV.

Table XIV

	Specific Conductivity $\times 10^{3}$		Concentration Moles per L. $\times 10^{3}$		Surface of Quartz Sq.Cms. $\times 10^{-3}$	Weight of Solution grams.	Moles adsorbed by Quartz. $\times 10^{7}$
	Before	After	Before	After*			
1,	.144066	.1440949	1.12144	1.12070	16.65	235.	1.73
2,	.105748	.105770	.82894	.82825	17.35	217.	1.89
H_2O	.00093033	.00105483	0	.0009615	17.35	234.	
H_2O	.00094583	.001039377	0		16.65	231.	

*Corrected for polluting effect by quartz.

The foregoing values on quartz are merely the upper limits. The assumption that the particles are perfect spheres in the calculation of the total surface, gives a value which is less than the value of the actual surface. The variation in temperature of the bath 0.01° C. also gives an increase of about 0.02 % over the possible maximum values given above.

If the maximum value for the adsorption by quartz is considered to be the value given above then the maximum adsorption that can be present in the quartz cell, Figure II, used in the conductivity measurements is shown in Table XV. It is assumed in this calculation that the actual surface of the walls of the cell is twice as large as the surface calculated from the diameter of the cell. This is done because the walls of the cell show irregularities and

pits and the surface calculated from the diameter undoubtably gives a low result. The maximum amount of the electrolyte that may be adsorbed at concentrations lower than .001 N is found by the use of the general adsorption equation:

$$\frac{X}{M} = K\, C^{1/n}$$

where X is the amount adsorbed, M is the number of grams of adsorbent or the surface and C is the concentration of the material adsorbed. K and n are characteristic empirical constants. The value of n varies between the limits 2 and 10.

Since the surface remains constant M and K can be united into a single constant K_1 and the equation becomes

$$X = K_1\, C^{1/n}$$

If the value calculated for X from the data above on adsorption at the concentration .0008283 equivalent per liter and the value of n be taken as 10 which may be assumed as giving a maximum value to X in the more dilute solutions, then K_1 can be evaluated. By the evaluation of K_1 the equation passes into the following form,

$$X = 4.7786 \times 10^{-8}\, C^{1/10}$$

From this equation the maximum amounts of potassium chloride that may be adsorbed by the cell are calculated. The maximum percentage errors which may be produced in the concentrations of the solution in the cell are also given.

Table XV

Calculated surface of cell = 1030 sq.cms.

Allowed surface of cell = 2060 sq.cms.

Volume of flask = 2.8 liters.

Concentration solution Moles per liter $\times 10^{6}$	Moles adsorbed on wall of cell $\times 10^{8}$	Maximum percentage error in concentrations.
10.	1.5	.053
20.	1.6	.028
50.	1.8	.013
100.	1.9	.0068

V

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

The Error in Λ_c

The accuracy to be expected in Λ_c may be estimated from a consideration of the errors in the elementary terms entering into this quantity. The equivalent conductance is calculated from the following equation:

$$\Lambda_c = \frac{1000\ \bar{L}}{C}$$

Resolving this equation into fundamental terms it becomes

$$\Lambda_c = \frac{1000 \times 74.56}{\delta} \cdot \frac{(\bar{L}_s - \bar{L}_w)\ W_{soln}}{W}$$

74.56 = Molecular weight of KCl.

δ = Density.

W = Weight of salt in grams.

W_{soln} = Weight of solution in kilograms.

$\bar{L}_s$ = Specific conductivity of solution = $\frac{1}{R_s}$

$\bar{L}_w$ = Specific conductivity of water = $\frac{1}{R_w}$

Substituting the term $\frac{1}{R_s}$ for $\bar{L}_s$ and $\frac{1}{R_w}$ for $\bar{L}_w$ and introducing K, the cell constant into the above equation it is converted into a form having only terms that are directly measured in the experiments and whose individual errors are known

$$= \frac{1000 \times 74.56}{\delta} \cdot \frac{K(1-\frac{R_s}{R_w})\ W_s}{W}$$

The errors in all these quantities are very small except in the case of the quantity W, the weight of the salt. This could not be obtained with a precision greater than .05%. Since the salt crystals had to be small in order to obtain a sufficiently high

EQUIVALENT CONDUCTANCE
.8
.7
.6
.5
.4
.3
.2
.1
129.0
.9
.8
128.7
0
25
50
75
100
125
150
175
200
225
1. FEB. 2.
2. JAN. 24
3. FEB. 24.
4. FEB. 10.
5. MAR. 6.
C. 10^6 MOLES PER LITER

Fig. C

dilution this error could not be avoided with the balance available. The above precision required that the crystal should be weighed and handled with an error not greater than 0.002 milligram. The sensibility of the balance accounted for a variation of 0.001 milligram in the weight of the salt. Another 0.001 milligram may be assigned to the error in the calibration of the weights and in the handling of the crystal.

The errors in R_s were limited by the accuracy of the Resistance Box calibration, 0.01%, for the precision of the bridge setting and ratio of arms was 0.00025%. R_w was measured to 0.1%. $1 - \frac{R_s}{R_w}$ has a maximum error of 0.02% i.e., at the lowest concentrations measured. The variation in the separate determination of the cell constant K was only .01%. The weighing of the solution was made with an accuracy of 0.001 %.

In comparison with the large error in W, the errors in the other measured quantities may be disregarded and the expected errors in the individual Λ_c values may therefore be taken as on the average not greater than 0.05%.

Consistency of Data

The data obtained in the conductivity runs are plotted in figure C, with the values of Λ_c as ordinates and the values of the corresponding concentrations as abscissas. The size of the diameter of the circle around each point is made equal to .05%, the expected error in the determination as explained above. Due to the experimental error of the determinations, the points for the separate runs do not lie on any single smooth curve. For the purpose of the calculations appearing in the discussion to follow, smooth curves were

constructed passing thru the points for each of the five runs. A set of Λ_c values at round concentrations was read off each of these curves. Of the five runs one of them that of March 6, seemed to be inconsistent with the four others. This inconsistency showed itself even by the inspection of Figure C and was more pronounced in the study of the limiting Λ_o values and the behavior of the mass law constants calculated from its values as described below. For these reasons the data obtained from the run of March 6th. are disregarded and the theoretical considerations to follow are based upon the values of Λ_c found in the four other runs.

The values of Λ_c taken off the smooth curves are given in Table XVI. The average of the values at round concentrations excluding the run of March 6th. are shown in the same table. It can be seen that in no case does a value taken from one of the curves deviate from the average value by more than about .025%.

Table XVI

Date	.000020 N	.000050 N	.000075 N	.0001 N
Jan. 24.	129.515	129.320	129.170	129.030
Feb. 2.	129.510	129.360	129.150	129.015
Feb. 10.	129.537	129.317	129.220	129.080
Feb. 24.	129.500	129.324	129.165	129.020
Mar. 6.	129.427	129.190	129.04	128.93
Average *	129.515	129.324	129.176	129.036

* March 6th. data not included in average.

Determination of the Λ_o value

The Λ_o value cannot be measured experimentally for it is the limiting value of Λ_c at zero concentration. Theory does not

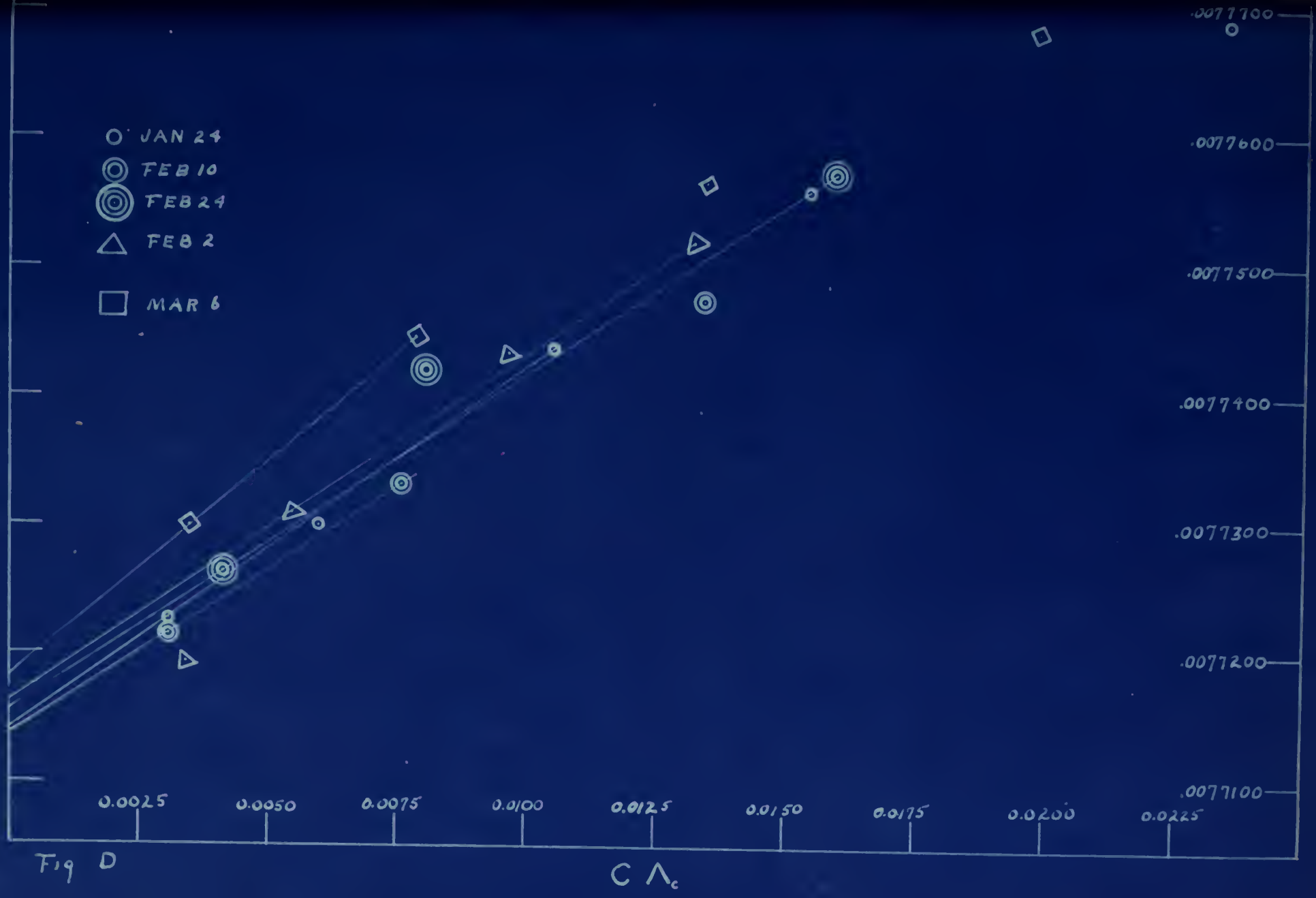

JAN 24
FEB 10
FEB 24
FEB 2
MAR 6
1/λc
.0077700
.0077600
.0077500
.0077400
.0077300
.0077200
.0077100
0.0025
0.0050
0.0075
0.0100
0.0125
0.0150
0.0175
0.0200
0.0225
C Λc

Fig D

afford a satisfactory method for calculating it. From accurate data at low concentrations however, upper and lower, limiting values of Λ_o may be calculated. These limiting values may be found by the analytical method of Bates (34) or by graphical extrapolation.

The lower limit of the Λ_o value is obtained by assuming that the Ostwald Dilution Law holds from the next to the lowest measured concentration down to zero concentration. This lower limit was actually found by plotting the values of $\frac{1}{\Lambda_c}$ against $C\Lambda_c$ for the two consistent points in the most dilute solutions for each "run" and extrapolating to zero concentration. These minimum values are tabulated in Table XVIII and shown graphically in Figure D.

The upper limit of Λ_o was determined in two ways; the graphical method and the analytical method. The graphical method gives higher results than the analytical. Essentially it consists in assuming that the functional relation between Λ_c and concentration which holds in dilute solutions continues to hold down to zero concentration. This upper value of Λ_o is actually found by superimposing two curves A and B, Figure E, made by plotting Λ_c as ordinates against C as abscissas in such a way that two points (m) and (n) of each curve coincide. In this case the point (m) represented aconcentration of .0002 N on curve B and 0.00002 N on curve A. The point (n) represented 0.0005 N on curve B and 0.00005 on curve A. Curve A has a concentration range .00005 N to .0, curve B .0005 N to 0. The ordinates for curve A are designated on the left hand margin. The scale of ordinates for curve B is so chosen that the point (m) on curve B coincides with m on curve A and so that the point (n) on curve B coincides with n on curve A. The ordinates at the right in brackets correspond to the concentrations on the

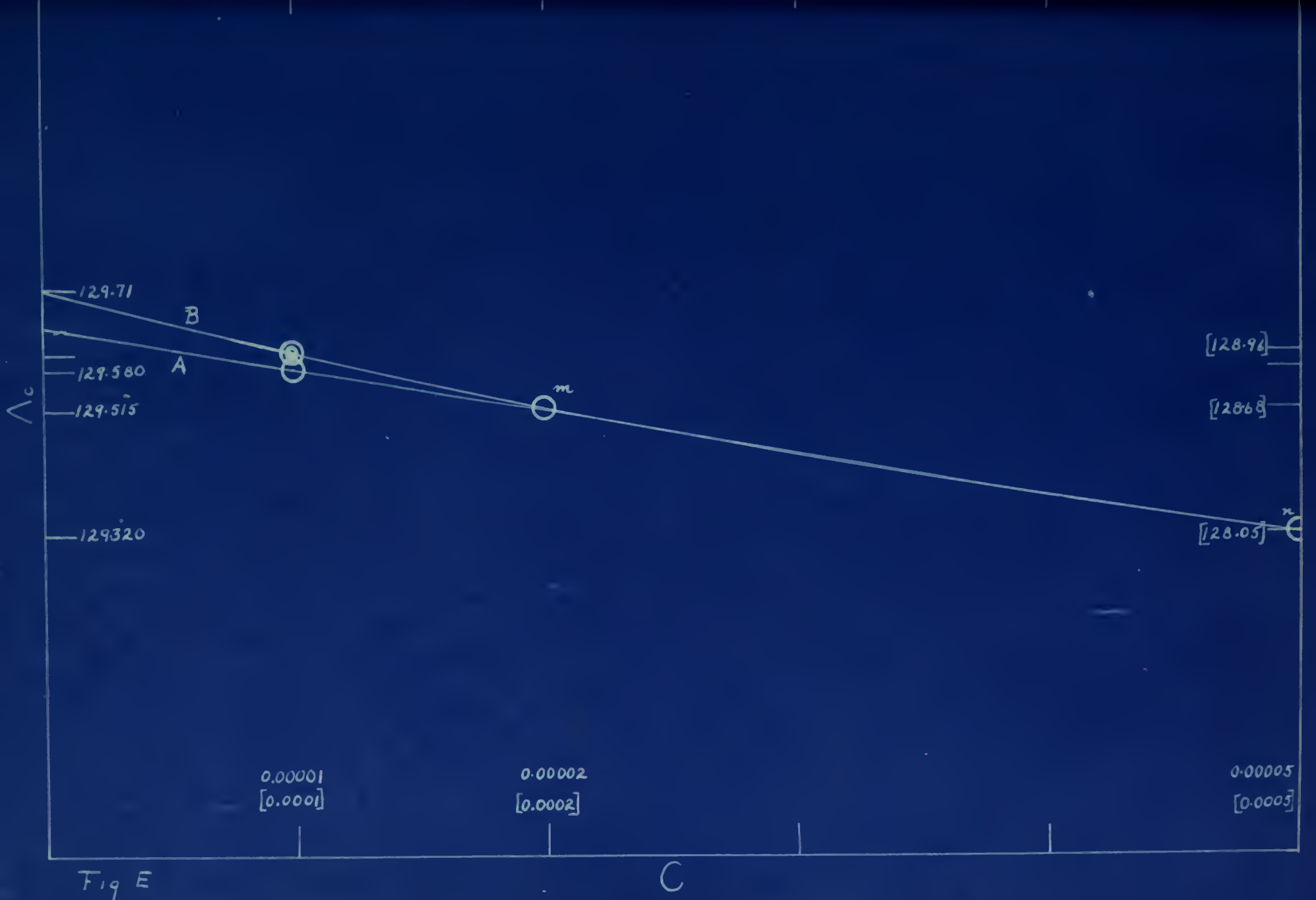

129·71
B
A
129·580
129·515
129320
m
n
[128·94]
[128·68]
[128·05]
0.00001
[0.0001]
0·00002
[0.0002]
0·00005
[0.0005]
C

Fig E

abscissas in brackets. The intercept of curve B at zero concentration, reading the ordinates on the left hand margin gives the upper limit of Λ_o.

Individual diagrams for each of the runs were made as described above. The upper limits as found are indicated in Table XVIII.

The analytical upper limit was obtained by the method of Bates, (35). Values of Λ_c were substituted in the following equation:

$$n \log \frac{C_1 \Lambda_1}{C_2 \Lambda_2} = \log \frac{C_1(\Lambda_o - \Lambda_1)}{C_2(\Lambda_o - \Lambda_2)}$$

where C_1 and C_2 represented a pair of the lowest concentrations, Λ_1 and Λ_2 the corresponding Λ_c values and then it was solved for (n). Three pairs of concentration ranges were chosen for each run using the values for Λ_c appearing in Table XVI. If the value of (n) reached a maximum, a new Λ_o value lower than the first was chosen and (n) was recalculated. This method was continued till (n) showed no maximum and the highest value of Λ_o fulfilling the above condition was used as the maximum value of Λ_o.

An example will serve to illustrate this method of calculation. The data chosen are from the Λ_c values shown in Table XVI for January 24th. The pairs of concentrations used are shown in column I of Table XVII. The values of (n) corresponding to the different values of Λ_o are shown in the other columns.

Table XVII

Concentration range	Λ_o=129.65	Λ_o=129.66	Λ_o=129.67
.000020-0.000050	1.979	1.922	1.880
0.000050-0.000075	1.932	1.906	1.883
0.000075-0.0001	1.900	1.885	1.86

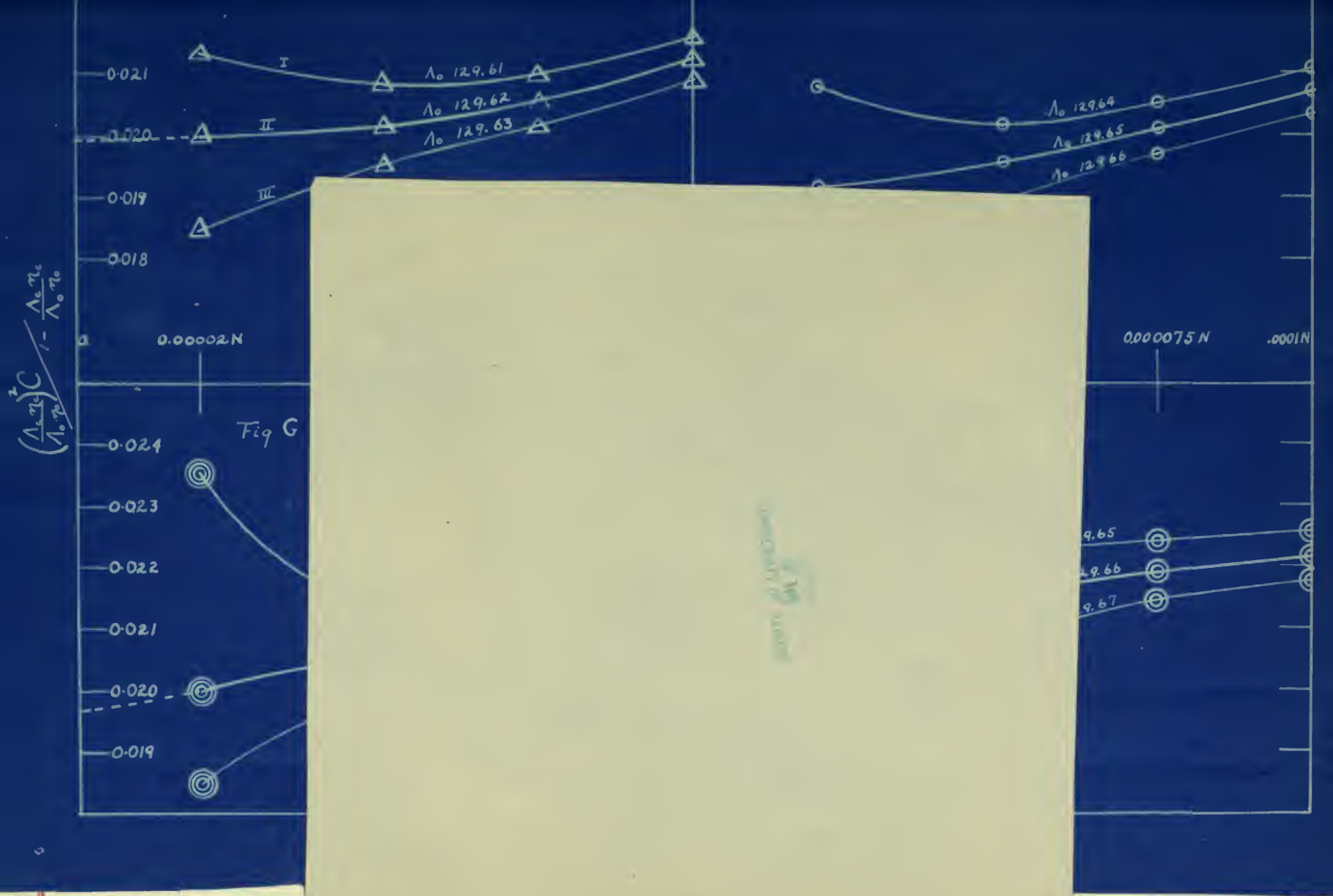
Using as Λ_o either 129.65 or 129.66 does not cause a maximum to appear. However when the value of Λ_o reaches 129.67 a distinct maximum shows itself. The value chosen as the upper limit in this case was 129.66 .

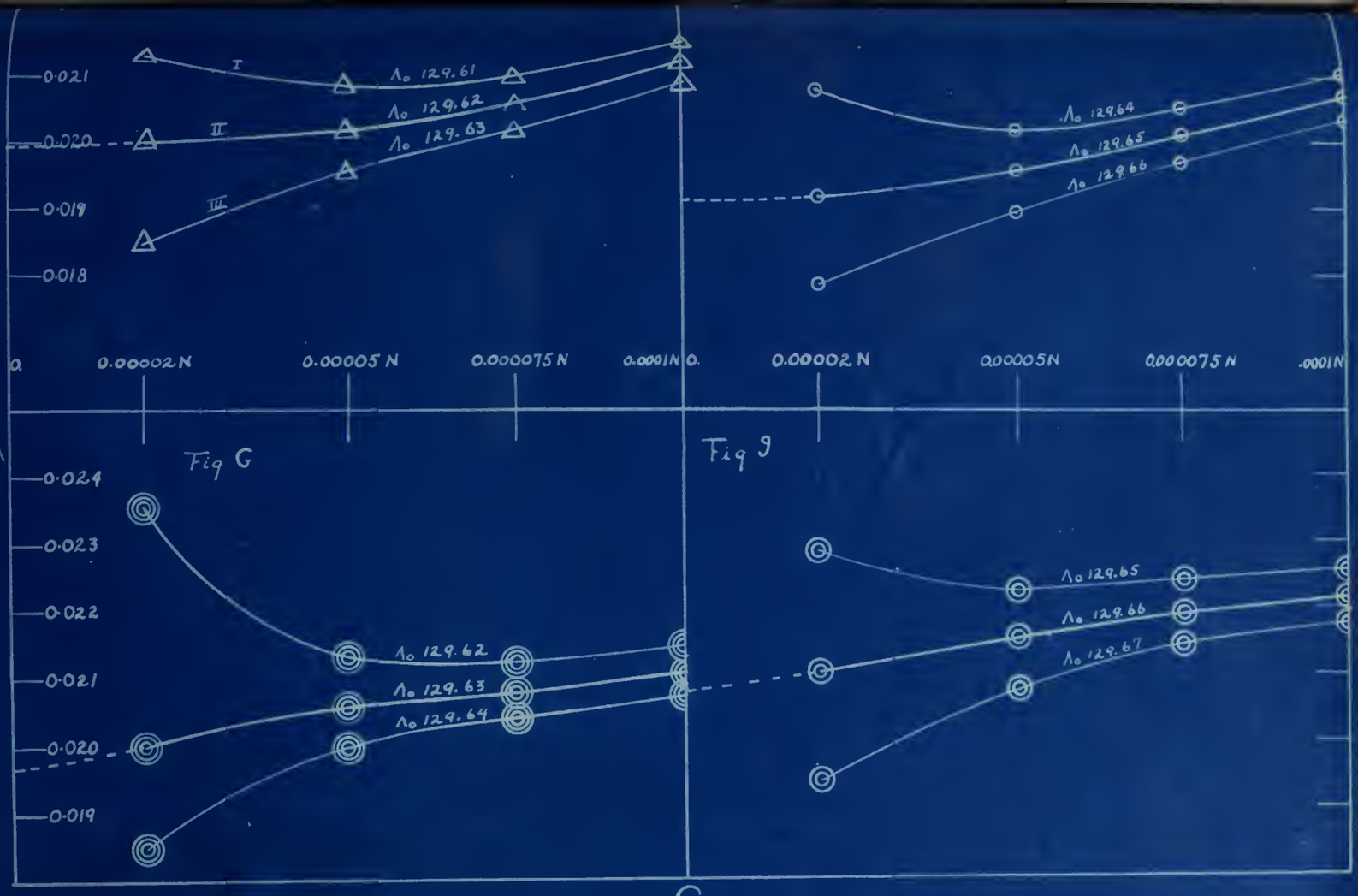
The upper analytical limit of each run has been calculated as above. The results of these calculations are shown in Table XVIII.

Table XVIII

	Analytical		Graphical
Date	Upper	Lower	Upper
Jan. 24.	129.66_6	129.63_4	129.71_0
Feb. 2.	129.63_5	129.59_6	129.71_0
Feb. 10.	129.65_0	129.64_3	129.73_0
Feb. 24.	129.62_0	129.60_9	129.71_0
March 6.	129.64_0	129.56_0	129.64_5

The final choice of the Λ_o value was based upon a study of its influence upon the calculated value of the equilibrium constant K_E . The variability of the mass law "constant" for a small change in the value of Λ_o is quite apparent in dilute solutions. This is due to the close dependence of the value of the term $1 - \frac{\Lambda_c}{\Lambda_o}$ upon the Λ_o value. The variability of $C\left(1 - \frac{\Lambda_c}{\Lambda_o}\right)$ with a change in Λ_o has already been referred to in Table I. The value of the equilibrium "constant" at zero concentration is not known but it will approach a definite limit in sufficiently dilute solutions. The changes in the value of K_E in very dilute solutions must be very small because the thermodynamic environment of the solution is altered but slightly by a small change in the concentrat-


0.021
0.020
0.019
0.018
I
II
III
Λo 129.61
Λo 129.62
Λo 129.63
Λo 129.64
Λo 129.65
Λo 129.66
0.00002N
0.0000075 N
.0001N
$\frac{(\Lambda_e \pi_e)^2 C}{\Lambda_o \pi_o} / 1 - \frac{\Lambda_e \pi_e}{\Lambda_o \pi_o}$
Fig G
0.024
0.023
0.022
0.021
0.020
0.019
9.65
9.66
9.67



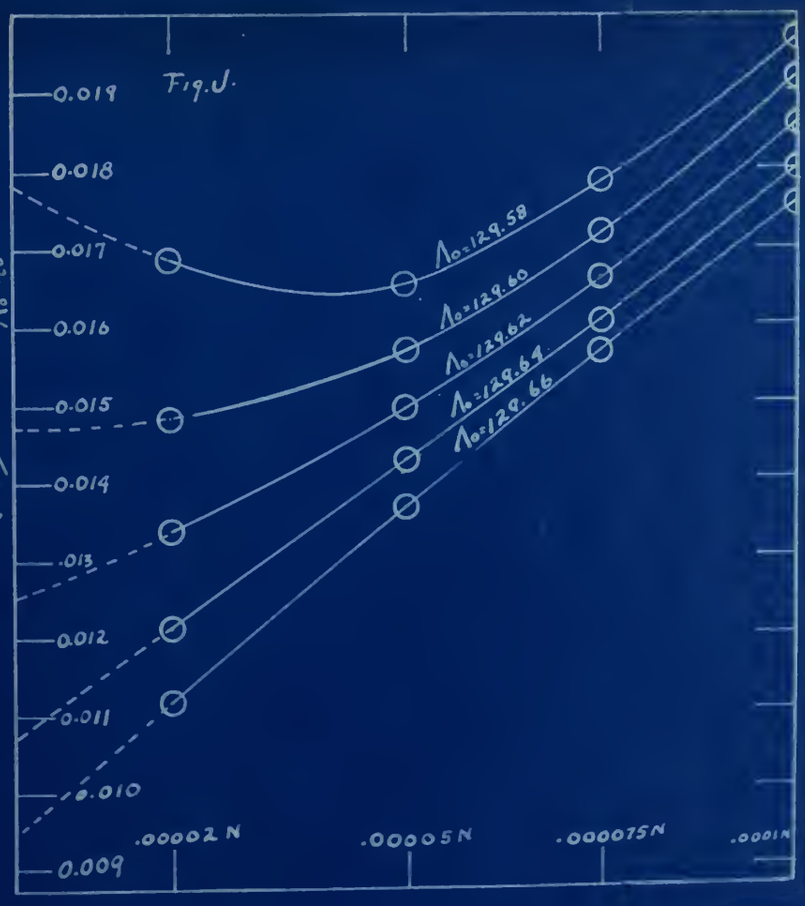
$$\left(\frac{\Lambda_c \pi_c}{\Lambda_o \pi_o}\right)^2 \frac{C}{1 - \frac{\Lambda_c \pi_c}{\Lambda_o \pi_o}}$$

Fig G

Fig I

C

Fig.J.



$$\left(\frac{\Lambda_c \pi_c}{\Lambda_o \pi_o}\right)^2 \frac{C}{1 - \frac{\Lambda_c \pi_c}{\Lambda_o \pi_o}}$$

ion. It is only sensible to assume under these conditions that the values of K_E when plotted as ordinates against the values of the corresponding concentrations as abscissas shall give a curve which gradually flattens out and at zero concentration becomes parallel to the concentration axis. A study of figures (L) and (M) shows this to be the case.

Plots were constructed for each of the individual runs having as abscissas the values of the concentration and as ordinates the values of K_E. The values of Λ_c for each run taken from Table XVI have been used with varying Λ_o values and the K_E value calculated by substituting these values in the equilibrium expression. These plots are shown in Figures F, G, H, I, J. It is to be noticed that the small change of 0.01 of a unit in the Λ_o value produces a decided change in the nature of the resulting curve. Considering Figure (F), it is not reasonable to assume that the true relation of K_E and C. could be represented in the dilute solutions by such rapidly changing curves as I and III. The true relation is expressed by curve II. Assuming that curve II is the nearest to the three in representing the true relation, then, the value for Λ_o of each run may be chosen rather exactly. The Λ_o chosen for each run by this method is shown below.

Table XIX

Date	Λ_o	Date	Λ_o
Jan. 24.	129.65_0	Feb. 24.	129.62_7
Feb. 2.	129.62_0	Average	129.63_8
Feb. 10.	129.65_5	March 6.	See Figure J.

By a careful weighting of the results calculated for the limiting values and the behavior of the equilibrium constants following a small change in the Λ_o value chosen, the final Λ_o value was fixed. The value chosen was 129.64 ± .02. The average value for the four runs was 129.638.

By an inspection of the four curves F, G, H, I, the value of K_E was taken as 0.020 ± .001 . The individual values of K_E taken off the curve at zero concentration were :

△	=.0199
○	=.0192
◎	=.0202
◎	=.0210
Average	=.0201

Λ_c values at round concentrations

Λ_c values at round concentrations were determined by the following method. A plot was made with Λ_c as ordinates and $C\Lambda_c$ as abscissas using the experimental values of all four runs. This plot extended from zero concentration to .001 N . It was made upon coordinate paper having ten squares to the inch, each inch square on the ordinate axis representing 0.1 reciprocal ohm. The range of the $C\Lambda_c$ values on the axis of the abscissas covered 70 inches. Three Λ_c values in the vicinity of .001 N had been determined in connection with some of the runs and from them the points at .001 N were fixed. These points checked the values found by Kohlrausch and Maltby (36) to .02%. The present Λ_c values at a concentration greater than .001 N are good.

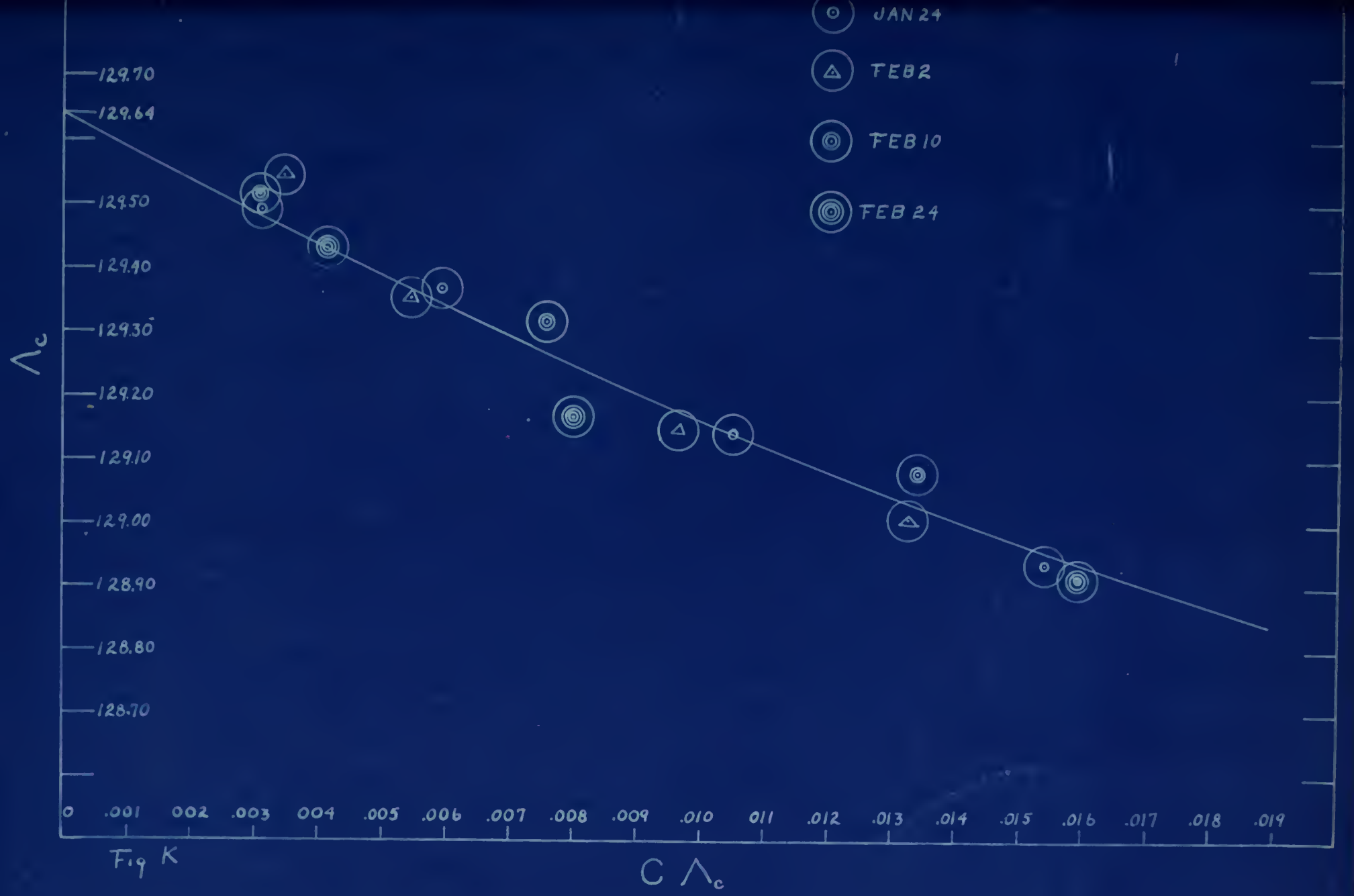

JAN 24
FEB 2
FEB 10
FEB 24
129.70
129.64
129.50
129.40
129.30
129.20
129.10
129.00
128.90
128.80
128.70
Λ_c
0
.001
002
.003
004
.005
.006
.007
.008
.009
.010
011
.012
.013
.014
.015
.016
.017
.018
.019
$C\Lambda_c$

Fig K

Table XX

Concentration Moles per L.	Λ_c
.00102187	127.22_4
.000958217	127.31_2
.00129902	126.86_9

The position of the curve passing thru the points in the dilute solution was so fixed that the Jan. 24th. and Feb. 2nd. data were given somewhat greater weight than the others. This was done because the values of K_E calculated from these sets of data were most consistent and agreed most closely with the value finally chosen for K_E at zero concentration- See Figures F, G, H, I, J.-.

The locus of the curve between .000020 N and zero concentration was fixed by the use of the values chosen for Λ_o and for K_E. This part of the curve is practically a straight line whose slope can be determined with the aid of the mass law. The value of $\frac{d\Lambda}{d(C\Lambda)}$ gives the slope of the curve in this region. This can be actually calculated by equating the mass law relation to the selected value of K_E at zero concentration and getting the first derivative of Λ with respect to C Λ . The mass law expression is

$$\frac{\left(\frac{\Lambda_c}{\Lambda_o}\right)^2 C}{1 - \frac{\Lambda_c}{\Lambda_o}} = K_E$$

or if this is rearranged and grouped so that the variables Λ_c and C Λ_c can be separated easily.

$$\frac{\Lambda_c\,(C\Lambda_c)}{\Lambda_o - \Lambda_c} = \Lambda_o K_E$$

For convenience let $y = \Lambda_c$, $x = C\Lambda_c$

then $$\frac{yx}{} = \Lambda_o K_E (\Lambda_o - y) = \Lambda_o^2 K_E - \Lambda_o K_E y$$

and $$\frac{dy}{dx} = \frac{-y}{x + \Lambda_o K_E}$$

at the limit where $x = o$

$$\frac{dy}{dx} = \frac{-y}{\Lambda_o K_E} = \frac{-\Lambda_o}{\Lambda_o K_E} = -\frac{1}{K_E}$$

If the value of K_E is taken as .020 then

$$\frac{dy}{dx} = -50$$

$$-\frac{\Delta \Lambda}{\Delta (C\Lambda)} = 50$$

By supplying the value of $\Delta (C\Lambda)$ for a point at a concentration in the vicinity of .00002 N the corresponding value of $(-\Delta\Lambda_c)$ may be found. A number of values of $\Delta (C\Lambda)$ were supplied in the final equation above and the resulting calsulated values of $(-\Delta\Lambda_c)$ were added to the Λ_o value. These points gave the locus of the curve in the immediate vicinity of zero concentration.

The entire plot of Λ_c against $C\Lambda_c$ is too large to be included here so that only the upper part extending from zero concentration to .00015 N is shown in Figure K. The values of Λ_c and the corresponding values of $\frac{C\Lambda_c}{1000}$ under the heading $\bar{L}$ are shown in Table XXl

In order to conveniently find the Λ_c value for a given round concentration, another plot was constructed having as ordinates Λ_c, as abscissas C. The values of C corresponding to any Λ_c were calculated from values of Λ_c and $C\Lambda_c$ taken off the curve in Figure K. The values of Λ_c at round concentrations are shown in Table XXI.

Table XXI

Concentration Moles per L.	$\bar{L} \times 10^6$ ±.02%	Λ_c ±.02%	$\alpha = \frac{\Lambda_c}{\Lambda_o}$	$\frac{\frac{\Lambda_c}{\Lambda_o} C}{1 - \frac{\Lambda_c}{\Lambda_o}}$	$1 - \frac{\Lambda_c}{\Lambda_o}$
0.0	.0	129.64	1.0000	0.020	0.0
.00001	1.2957_6	129.57_6	$.9995_0$	$.020_2$	$.00049_5$
.00002	2.5902_2	129.51_1	$.9990_0$	$.0200_6$	$.00099_9$
.00003	3.8834_1	129.44_7	$.9985_1$	$.0200_9$	$.00148_9$
.00004	5.1753_6	129.38_4	$.9980_3$	$.0202_8$	$.00197_5$
.00005	6.4661_5	129.32_3	$.9975_6$	$.0203_5$	$.00244_6$
.00006	7.7558_4	129.26_4	$.9971_0$	$.0205_6$	$.00290_1$
.00007	9.0443_5	129.20_5	$.9966_4$	$.0207_8$	$.00335_6$
.00008	10.332_0	129.15_0	$.9962_2$	$.0210_0$	$.00378_0$
.00009	11.618_7	129.09_7	$.9958_1$	$.0213_1$	$.00418_9$
.0001	12.904_8	129.04_8	$.9954_3$	$.0216_9$	$.00456_7$
.0002	25.736_0	128.68_0	$.9926_0$	$.0266_1$	$.00740_6$
.0003	38.530_5	128.43_5	$.9907_0$	$.0316_7$	$.00929_5$
.0004	51.292_0	128.23_0	$.9891_2$	$.0359_8$	$.01087_7$
.0005	64.021_0	128.04_2	$.9876_7$	$.0395_7$	$.01232_7$
.0006	76.722_6	127.87_1	$.9963_6$	$.0427_5$	$.01365_3$
.0007	89.397_0	127.71_0	$.9851_1$	$.0456_3$	$.01488_8$
.0008	102.04_1	127.55_1	$.9838_9$	$.0480_6$	$.01611_4$
.0009	114.66_0	127.40_0	$.9827_2$	$.0503_0$	$.01727_9$
.001	127.25_8	127.25_8	$.9816_3$	$.0524_4$	$.01837_4$

Behavior of Potassium chloride with respect to the Mass Law

In figures L, M, the mass law constants $\frac{\left(\frac{\Lambda_c}{\Lambda_o}\right)^2 C}{1 - \frac{\Lambda_c}{\Lambda_o}} = K_\varepsilon$ have been plotted as ordinates against the concentration as abscissas. Figure M shows a small portion of figure L magnified about five fold. The figures were made to demonstrate the relative

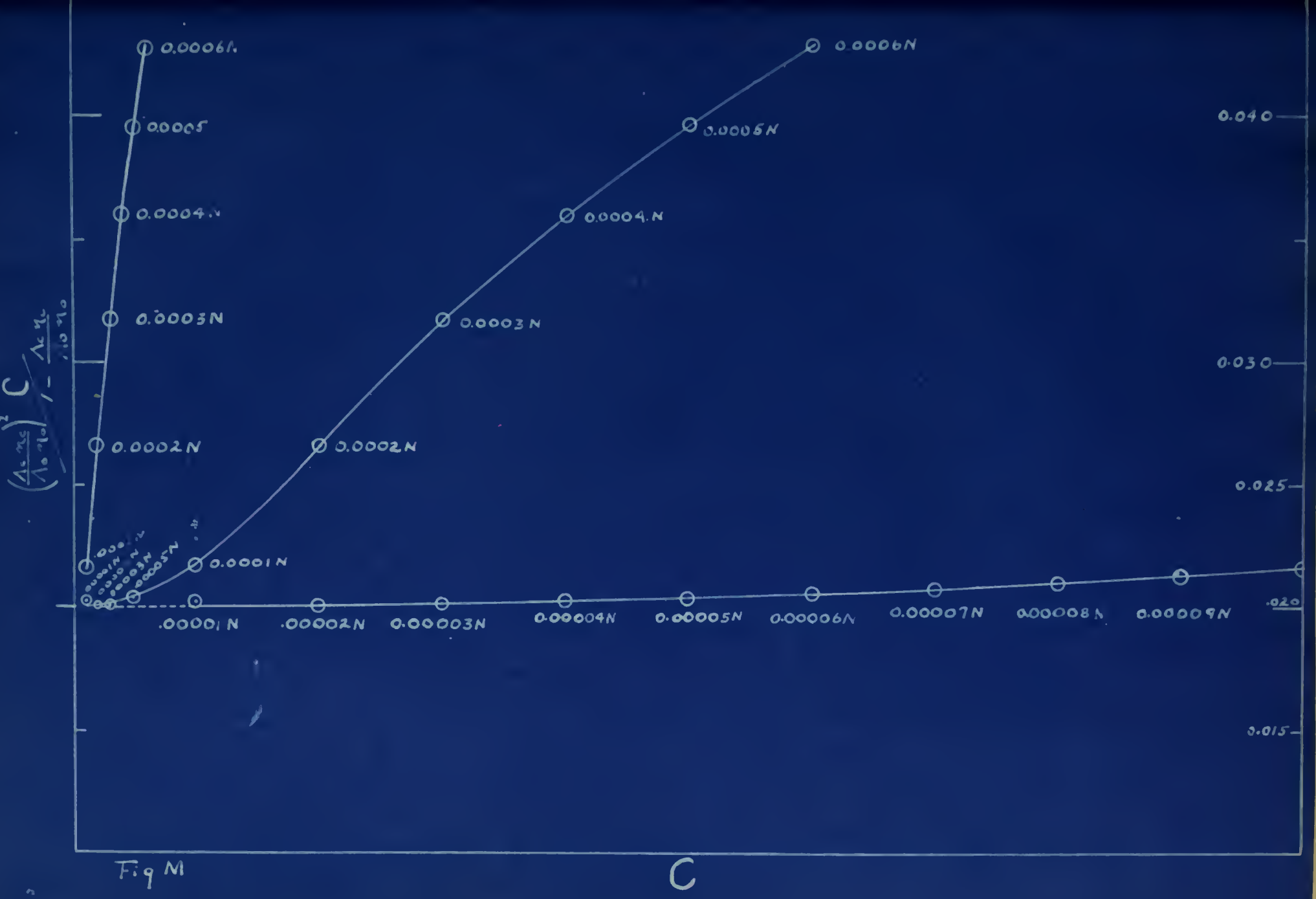

0.00006N
0.0005
0.0004N
0.0003N
0.0002N
0.0001N
0.00005N
0.00004N
0.00003N
0.00002N
0.00001N
0.0006N
0.0005N
0.0004N
0.0003N
0.0002N
0.0001N
0.040
0.030
0.025
0.020
0.015
.00001N
.00002N
0.00003N
0.00004N
0.00005N
0.00006N
0.00007N
0.00008N
0.00009N
$\left(\frac{\Lambda_c}{\Lambda_0}\right)^2 C \Big/ 1 - \frac{\Lambda_c}{\Lambda_0}$
C

Fig M

0.005 N
0.002 N
0.001 N
0.0005 N
0.0002 N
0.0001 N
0.00005
0.000001 N
0.00002 N
0.005 N
0.002 N
0.001 N
0.0005 N
0.0002 N
0.00005 N
0.000 N
0.11
0.10
0.09
0.08
0.07
0.06
0.04
0.03
0.01

Fig L

change in the value of K_E with a ten fold change of concentration in different parts of the concentration range. In the concentrated solutions this change in K_E with a ten fold change in concentration amounts to several hundred percent. As the solutions become more and more dilute the change in K_E becomes less and less until in the most dilute solutions K_E becomes practically constant. These changes in K_E with a ten fold change in concentration are given in Table XXII.

Table XXII

C_1 Moles per liter	C_2 Moles per liter	$\frac{K_{E_{C_1}}}{K_{E_{C_2}}}$
1.	0.1	4.05
0.1	0.01	3.34
0.01	0.001	2.68
0.001	0.0001	2.46
0.0001	0.00001	1.08

The Ostwald Dilution Law becomes a true relation for potassium chloride when the concentration of the solution is sufficiently dilute.

Upon consideration of the well known equations which are intended to express the relation between Λ_c and C, viz; the Bates equation. $\log_{10} \frac{\left(\frac{\Lambda_c n_c}{\Lambda_o n_o}\right)^2 C}{1 - \frac{\Lambda_c n_c}{\Lambda_o n_o}} = K + k' \left(\frac{C \Lambda_c}{\Lambda_o}\right)^k$ and the Kraus equation $\frac{\left(\frac{\Lambda_c n_c}{\Lambda_o n_o}\right)^2 C}{1 - \frac{\Lambda_c n_c}{\Lambda_o \eta_o}} = K + k' \left(\frac{C \Lambda_c}{\Lambda_o}\right)^k$ it can be shown by the use of the data in dilute solution that they

cannot express the relation over the entire concentration range.

The Bates equation can be transformed into the following form $\log K_E = K + k' \left(\frac{C\Lambda_c}{\Lambda_o}\right)^h$

or letting K = log Ⓚ and taking the logarithm of both sides the above becomes

$$\log \left(\log \frac{K_E}{Ⓚ}\right) = \log k' + h \log \frac{C\Lambda_c}{\Lambda_o}$$

In this equation $\text{Log}\left(\log \frac{K_E}{Ⓚ}\right)$ is a linear function of $\log C\Lambda$. A plot of this using the value of $\log \left(\log \frac{K_E}{Ⓚ}\right)$ as ordinates against log C Λ as abscissas should give a straight line if the function expresses the data. Values of the two variables were calculated over a concentration range .005 N to .00002 N. and the resulting values were plotted as described. From figure N it can be seen that curve (1) is not a straight line. The slope (h) of the curve is not constant over any part of the concentration range included in the figure.

In like manner the equation of Kraus can be shown to be the wrong function for expressing the relation of Λ_c to C in dilute solutions. It can be transformed as follows:

$$K_E = K_o + k' \left(\frac{C\Lambda_c}{\Lambda_o}\right)^h$$

or $$K_E - K_o = k' \left(\frac{C\Lambda}{\Lambda_o}\right)^h$$

Taking the logarithm of both sides

$$\log (K_E - k_o) = \log k' + h \log \frac{C\Lambda}{\Lambda_o}$$

In this equation log $(K_E - K_o)$ becomes a linear function of log C Λ . The graph of this equation with log C Λ as abscissas and log $(K_E - K_o)$ as ordinates, designated at right hand margin is shown

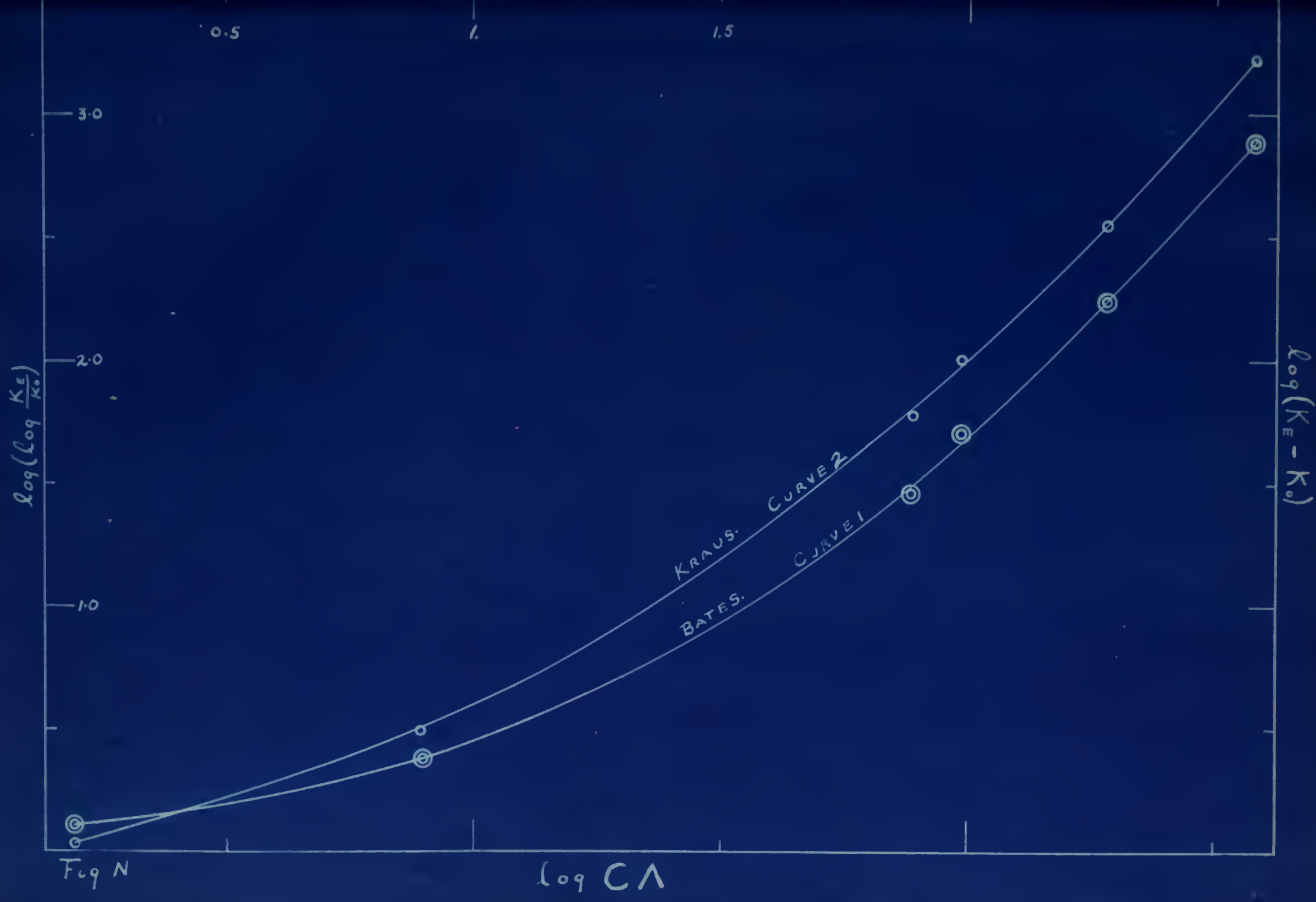

0.5
1.
1.5
3.0
2.0
1.0
log (log Kε/K₀)
log (Kε - K₀)
KRAUS. CURVE 2
BATES. CURVE 1
log CΛ

Fig N

in figure N. The values plotted represent a concentration range from .005 N to .00002 N. The resulting curve (2) is obviously not a straight line.

The data used for the construction of figure N are shown in Table XXIII.

Table XXIII

Concentration Moles per L.	$C\Lambda$	K_E	K_E/K_o	(K_E-K_o)	$-\log(C\Lambda)$	$-\log(\log\frac{K_E}{K_o})$	$-\log(K_E-K_o)$
.005	.62165	.11215	5.607	.09215	.20645	0.12567	1.0355
.001	.127258	.052443	2.6221	.03244	.89531	0.37817	1.4889
.0001	.0129048	.021696	1.0848	.001696	1.8892	1.4516	2.7706
.00008	.0103320	.021004	1.0502	.001004	1.9858	1.6723	2.9983
.00004	.00517536	.020275	1.0137	.000275	2.2861	2.2285	3.5606
.00002	.00259022	.02006	1.0030	.00006	2.5866	2.8857	4.2218

VI

SUMMARY

SUMMARY

I. Conductivity water with a specific conductivity of $(.053 - .070) \times 10^{-6}$ at 18° C has been prepared in large quantities by a single distillation of ordinary conductivity water from a quartz still into a quartz cell. This distillation was carried out in air free from carbon dioxide and ammonia.

II. A quartz cell, about three liters capacity provided with electrodes in the form of two coaxial platinum cylinders and so constructed that nothing but quartz or platinum shall come in contact with the water, has been designed and constructed for the measuring of the conductivity of the water and the salt solutions prepared in it.

III. Potassium chloride solutions ranging in concentration from .00002 N to .001 N have been prepared in this conductivity water out of contact with the atmosphere by the successive introduction into the cell of small crystals of salt weighing about .005 grams. The electrical conductivities of these solutions have been measured and their equivalent conductances calculated.

IV. In order to ascertain the magnitude of the concentration change due to the adsorption of the salt on the walls of the cell, the specific adsorption of potassium chloride was determined by the use of a large quantity of quartz fragments. This study consisted in observing the conductivity of .001 N to .0005 N solutions of potassium chloride in a special quartz cell before and after the addition of a definite quantity of well cleaned quartz fragments. Knowing the magnitude of the surface of the fragments and the surface of the cell, the maximum concentration change resulting from adsorption has been calculated.

V. The values of the equivalent conductance of potassium

chloride over the concentration range .00002 N to .001 N have been determined experimentally. By a study of the data in the most dilute solution, upper and lower limiting values of Λ_o in each run have been fixed. The behavior of the mass law "constant" as a result of very small changes in the Λ_o value for each run, together with the limiting values furnished a means for determining the Λ_o value with a maximum uncertainty of 0.01%. The final value for Λ_o was taken as 129.64 ± .02, the average of the Λ_c from the four individual runs being 129.638.

The values of Λ_c at round concentrations have been tabulated over the concentration range .00001 N to .001 N.

VI. The value of the equilibrium "constant" K_E has been found to approach a constant value as the solution becomes sufficiently dilute. The limiting value at zero concentration was chosen as .020 ± .001, the average of the four runs being .020 . The relative increase of K_E for a ten fold increase in concentration over different regions of the concentration range has been demonstrated graphically in figures L and M.

VII. The empirical equations of Bates and of Kraus and Bray intended to express the relation between equivalent conductance and concentration have been tested between concentration range zero and .005 N and have been found not to be capable of expressing the conductivity data in this region.

VII

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BIBLIOGRAPHY

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VIII

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ACKNOWLEDGMENT

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IX

BIOGRAPHICAL

BIOGRAPHICAL

The writer received his elementary and secondary education in the Rochester Athenaeum and the public schools of Rochester, New York. He entered the University of Rochester in the fall of 1909 and was graduated with the degree of Bachelor of Science in 1913. During the college years 1913-17 he has been a graduate student in chemistry at the University of Illinois, receiving the degree of Master of Science in 1915.

He was a graduate assistant in general chemistry, 1913-14; assistant chemist Illinois State Water Survey, summer of 1914; research assistant in physical chemistry, 1914-16; assistant in quantitative chemistry 1916-17.

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